Japanese Kokai Patent Application No. Sho 60[1985]-239739

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KOKAI PATENT APPLICATION NO. SHO 60[1985]-239739

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A RECORDING MEDIUM

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[There are no amendments to this patent.]

Claim

A recording medium characterized by the fact that a monomolecular film or a monomolecular layer built-up film of an enclosure complex, formed of a host molecule, possessing a hydrophilic site, hydrophobic site and enclosure site therein, and a guest molecule to be enclosed in said host molecule, is formed on a support, thereby functioning as a recording layer.

Detailed explanation of the invention

1. Technical field

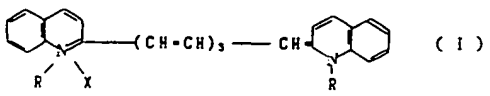
The present invention concerns a recording medium, with which recording is conducted by using the chemical change or physical change of a monomolecular film or a monomolecular layer built-up film of an enclosure complex.

2. Background of the technology

It has been known in the past that various organic compounds can be used as a recording medium in the form of a recording layer.

For example, an organic compound is employed as an optical recording medium, involving the formation of a thin film, which is then used as a recording layer, as disclosed in Japanese Kokai Patent Application No. Sho 56[1981]-16948 and Japanese Kokai Patent Application No. Sho 58[1983]-125246. In all cases, the disclosure concerns a laser recording medium, wherein an organic dye is used to form a recording layer, and recording regeneration is conducted by means of a laser beam. In particular, the medium disclosed in Japanese Kokai Patent Application No. Sho 58[1983]-125246 involves the use of a thin film of a cyanine dye (see general formula I) as a recording layer.

General formula (I)



(I)

A rotating coating device or the like is used to apply a solution of a cyanine dye as shown by general formula I onto a plastic support at a thickness not exceeding 1000 Å (e.g., a thickness of approximately 300 Å), thereby forming a thin film. If the molecular orientation in the film is random, light scattering occurs inside the film as it is being irradiated. When viewed microscopically, the degree of chemical reaction generated in correspondence with the degree of light irradiation varies. Accordingly, as a recording medium, it is desired that the molecular orientation of the film be ordered and that the film be as thin as possible, so that high-density recording requirements can be met. However, with coating methods, the film thickness limit is 300 Å, and the problem of random molecular orientation in the film cannot be solved.

It was disclosed in Japanese Kokai Patent Application No. Sho 56[1981]-42229 and Japanese Kokai Patent Application No. Sho 56[1981]-43220 that diacetylene compound built-up films proposed for use as a resist material with a large light quantum-photon effect and excellent resolution can be used not only as a resist material, but also can be applied in areas such as thin film electrical-optical devices, electrical-sound devices and pressure-pyroelectrical devices.

Recently, means for improving methods of manufacturing diacetylene compound built-up films were disclosed in Japanese Kokai Patent Application No. Sho 58[1983]-111029. According to this invention, a diacetylene compound built-up film on a manufactured support is caused to polymerize by means of ultraviolet light irradiation, thereby forming a diacetylene compound polymeric film; or a diacetylene compound built-up film

on a manufactured support is masked and partially/polymerized by means of ultraviolet light irradiation, which is followed by removing the nonpolymerized portion, thereby forming a pattern, so that the resulting material can be used as thin-film optical devices and integrated circuit elements.

However, all of these means are limited to diacetylene compounds, and the disclosure did not describe the possibility of erasing recorded data when it is used as a thin-film optical device.

Meanwhile, an optical recording medium was disclosed in Japanese Kokai Patent Application No. Sho 58[1983]-190932 for solving the above-mentioned shortcomings, wherein an optical recording medium that can be used repeatedly is characterized by the fact that a monomolecular film or monomolecular layer built-up film of a photopolymerizable monomer, possessing a hydrophilic group, hydrophobic group and at least one unsaturated bond in the molecule, is formed on a support, thereby forming a recording layer.

These diacetylene compound built-up films, as well as these monomolecular films or monomolecular layer built-up films of a photopolymerizable olefin monomer, involve a method of manufacturing in which a hydrophilic group and a hydrophobic group are introduced into a photoreactive compound, which is then directly applied onto a support. Accordingly, various functional films cannot be manufactured easily. Additionally, the addition of a hydrophilic group and hydrophobic group can bring about a decrease in photoreactivity. Moreover, another problem is that extremely complicated operations are required for controlling the orientation of the molecules on the film surface, which is

important in conducting a very high degree of high-density recording.

As a result of conducting studies on various methods for alleviating the shortcomings of the prior art, the inventors arrived at the present invention. The methods studied were (1) methods for manufacturing various functional films in a comparatively simple manner, (2) methods for forming a film in such a manner that the various functions possessed by the functional molecule are not damaged or reduced, even under conditions of forming a thin film, and (3) methods with which the film-constituting molecules form a highly ordered structure along a direction on the film surface, without having to conduct special operations during the formation of a thin film described above. Also, the present invention arrived at by the inventors can offer a high-sensitivity, high-resolution recording medium easily and with high quality, when these film-forming methods are used.

3. Disclosure of the invention

The objective of the present invention is to offer a high-density recording medium, wherein a chemical change or physical change is brought about by an external factor.

Another objective of the present invention is to offer a medium, which is better than that of prior art from the standpoint of the orientation of the molecules on the medium surface, which is an important factor for conducting high-density recording involving these molecules. Additionally, another objective of the present invention is to offer media with various

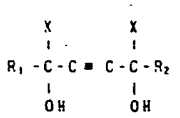
properties by altering the comparatively simple operations employed in the manufacture of the above-mentioned recording medium.

The above-mentioned objectives of the present invention are achieved with the present invention described below.

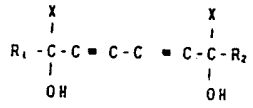
The present invention offers a recording medium characterized by the fact that a monomolecular film or a monomolecular layer built-up film of an enclosure complex, formed of molecules (host molecules), possessing a hydrophilic site, a hydrophobic site and a site that can enclose other molecules (enclosure site) therein, and molecules of another kind to be enclosed in said host molecules (guest molecules), is formed on a support, thereby functioning as a recording layer.

The material used to form the recording layer of the present invention is formed of two kinds of molecules, wherein the molecules of one kind each possess a hydrophilic site, a hydrophobic site and at least one site that can enclose other molecules (herein referred to as host molecules) and the molecules of another kind each can be enclosed by said host molecules (guest molecules). The recording medium of the present invention is formed by forming a monomolecular film or a monomolecular layer built-up film of an enclosure complex, formed of the above-mentioned host molecules and guest molecules, onto a support. However, it is required that one or both of these two kinds of molecules can be altered chemically or physically by an external factor, such as light, heat, electricity or magnetism. Specifically, recording of the recording medium of the present invention is conducted by utilizing the above-mentioned chemical change or physical change.

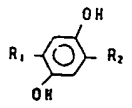
The host molecule used in the present invention can be any molecule that possesses a hydrophilic site, a hydrophobic site and at least one site that can enclose molecules of another kind, situated appropriately therein, as described above. Various commonly known typical hydrophilic groups and hydrophobic groups are representative examples of constituting elements with which the hydrophilic site and hydrophobic site in the molecule can be formed. The site, with which an enclosure complex with molecules of another kind can be formed, can be made by introducing a hydroxy group, carbonyl group, carboxyl group, ester group, amino group, nitrile group, thio group, imino group or the like. The above-mentioned host molecules are described specifically below, using examples of host molecules possessing hydroxy groups, as shown by general formulas IIa-IIc.



(II a)



(II b)



(II c)

(In these formulas, X = H or C_6H_5.)

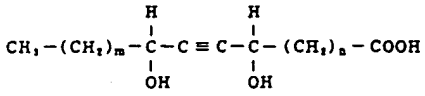
Specifically, it can be said that possessing a hydrophilic site and a hydrophobic site means that, for example, according to the above-mentioned formulas, a hydrophilic site is present on either R_1 or R_2, with a hydrophobic site present on the other, or that R_1 and R_2 exhibit hydrophilicity or hydrophobicity in relationship with the remaining part [of the molecule] other than

[R_1 and R_2]. Regarding the structure of R_1 and R_2, C_5-C_{30} long-chain alkyl groups are particularly preferred for introducing a hydrophobic site, and C_1-C_{30} fatty acids are preferred for introducing a hydrophilic group.

More specific examples of compounds that can be employed as the host molecule of the present invention include acetylene diol derivatives (nos. 1-6 and nos. 16-21), diacetylene diol derivatives (Nos. 7-12 and nos. 22-27) and hydroquinone derivatives (no. 13-15 and nos. 28-30). Also, in the following examples, m and n indicate positive integers, Z indicates $-CH_3$ or $-COOH$, and Ph indicates $-C_6H_5$.

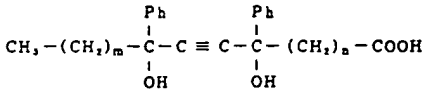
(Examples of acetylene diol derivatives)

No. 1



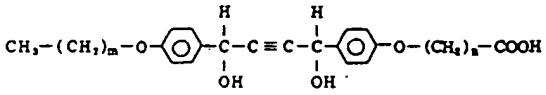
$30 \geq m + n \geq 11,\ n \geq 0$

No. 2



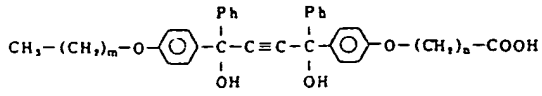
$30 \geq m + n \geq 11,\ n \geq 0$

No. 3



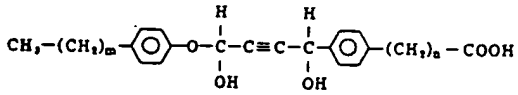
$30 \geq m + n \geq 8,\ n \geq 1$

No. 4



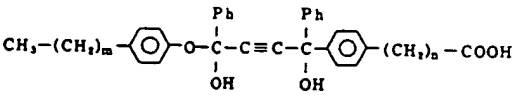
$30 \geq m + n \geq 8,\ n \geq 1$

No. 5



$30 \geq m + n \geq 8,\ n \geq 0$

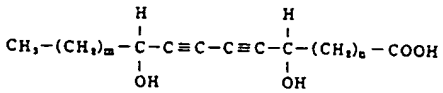
No. 6



$30 \geq m + n \geq 8,\ n \geq 0$

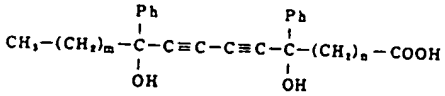
(Examples of diacetylene diol derivatives)

No. 7



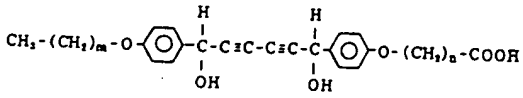
$30 \geq m + n \geq 9, \quad n \geq 0$

No. 8



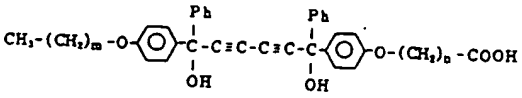
$30 \geq m + n \geq 9, \quad n \geq 0$

No. 9



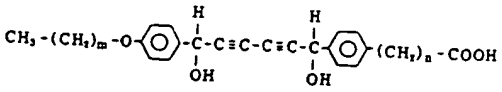
$30 \geq m + n \geq 5, \quad n \geq 1$

No. 10



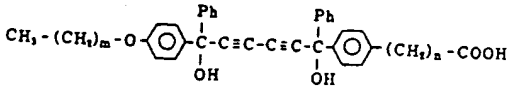
$30 \geq m + n \geq 5, \quad n \geq 1$

No. 11



$30 \geq m + n \geq 5, \quad n \geq 0$

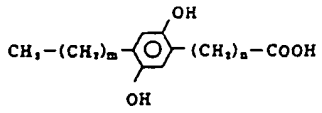
No. 12



$30 \geq m + n \geq 5, \quad n \geq 0$

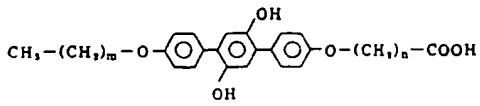
(Examples of hydroquinone derivatives)

No. 13



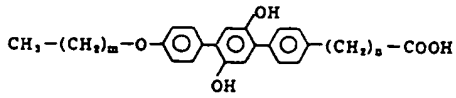
$30 \geq m + n \geq 13$, $n \geq 0$

No. 14



$30 \geq m + n \geq 9$, $n \geq 1$

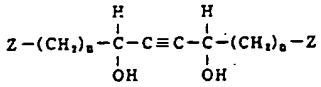
No. 15



$30 \geq m + n \geq 9$, $n \geq 0$

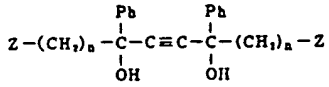
(Examples of acetylene diol derivatives)

No. 16



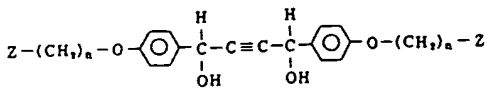
$30 \geq n \geq 5$

No. 17



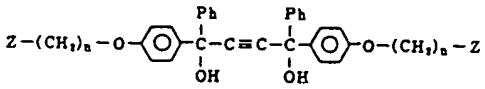
$30 \geq n \geq 5$

No. 18



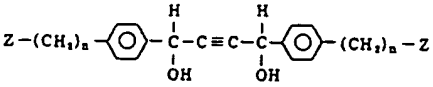
$30 \geq n \geq 4$

No. 19



$30 \geq n \geq 4$

No. 20



$30 \geq n \geq 4$

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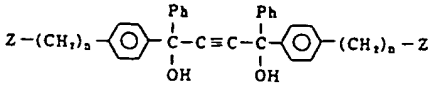
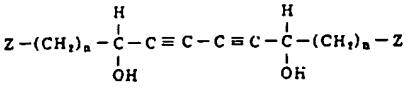


$30 \geq n \geq 4$

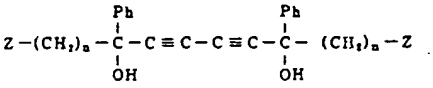
(Examples of diacetylene diol derivatives)

No. 22



$30 \geq n \geq 3$

No. 23



$30 \geq n \geq 3$

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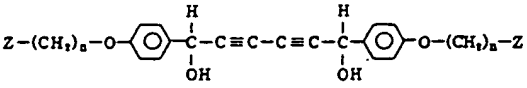
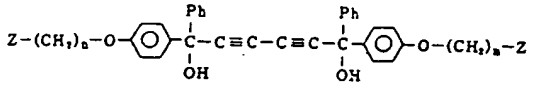


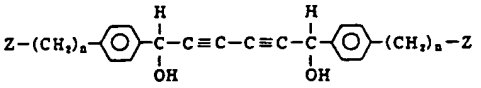
$30 \geq n \geq 1$

No. 25



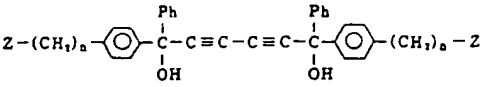
$30 \geq n \geq 1$

No. 26



$30 \geq n \geq 1$

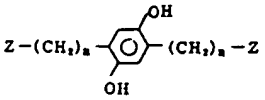
No. 27



$30 \geq n \geq 1$

(Examples of hydroquinone derivatives)

No. 28



$30 \geq n \geq 5$

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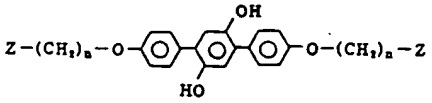
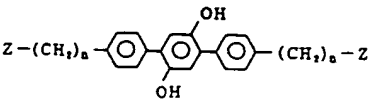


$30 \geq n \geq 1$

No. 30



$30 \geq n \geq 1$

Other than the fact that a long-chain alkyl group or a long-chain carboxylic acid group is substituted into the host molecule to bring about the introduction of hydrophilicity and hydrophobicity, the compounds cited above are commonly known compounds. Additionally, the subject of host molecules not modified with a long-chain alkyl group or the like forming a crystalline enclosure complex with various guest molecules has been described in the Journal of the Japanese Chemical Society, No. 2, p. 239-242 (1983).

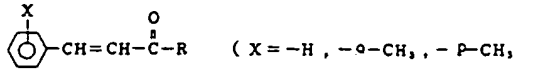
It is typically preferred that the guest molecule used to obtain an enclosure complex with the above-mentioned host molecules be a molecule that can form a strong hydrogen bond with the host molecule. Accordingly, as described above, when the host molecule possesses hydroxy groups as the enclosure site, an aldehyde, ketone, amine, sulfoxide or the like is employed as the guest molecule. Also, besides the above-mentioned compounds, the guest molecule can also be selected from various halogenated compounds or compounds with a π-electron system (i.e., alkenes, alkynes and allenes). In all cases, molecules with which the formed enclosure complex can possess a structure that exhibits the desired recording functions are selected.

Next, specific examples of guest molecules that can be employed for various functions are presented.

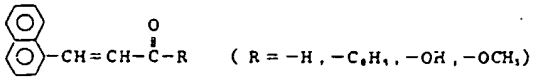
(1) Specific examples of guest molecules that can be employed in an optical recording medium, involving the dimerization reaction of the guest molecules, include olefinic compounds (nos. 31-34), diolefinic compounds (nos. 35-38), anthracene derivatives (no. 39) and 2-aminopyridiniums (no. 41).

(Examples of olefinic compounds)

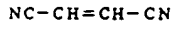
No. 31



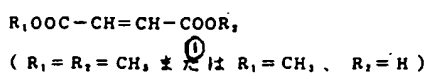
No. 32



No. 33



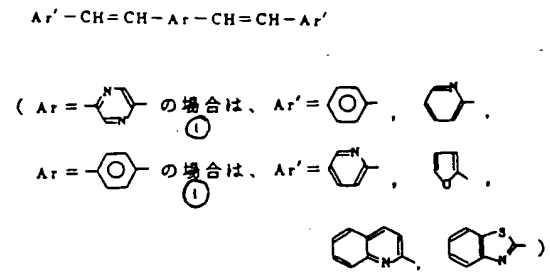
No. 34



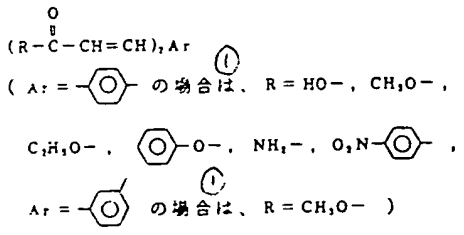
Key: 1 Or

(Examples of diolefinic compounds)

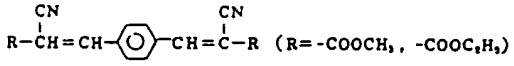
No. 35



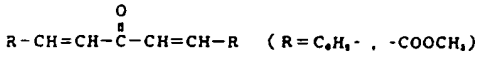
No. 36



No. 37



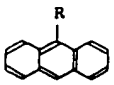
No. 38



Key: 1 For

(Examples of anthracene derivatives)

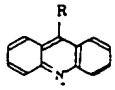
No. 39



(R = CH_3-, CHO-, -$COOC_2H_5$, Br-)

(Examples of acridinium derivatives)

No. 40



· X^- (R = -H, -CH_3, -C_2H_5,

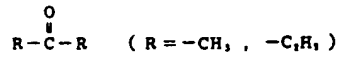
X^- = I^-, Br^-, Cl^-)

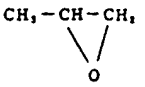
(2-aminopyridinium)

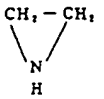
No. 41

· X^- (X^- = Cl^-, Br^-, I^-)

(2) Specific examples of guest molecules that can be employed in a recording medium, involving the sublimation of the guest molecules, include ketones (no. 42), epoxides (e.g., 1,2-epoxypropane) (no. 43), ethylenimine (no. 44), benzene (no. 45), chlorinated compounds (e.g., dichloromethane and chloroform) (nos. 46 and 47) and brominated compounds (e.g., methyl bromide) (no. 48).

No. 42 

No. 43 

No. 44 

No. 45

No. 46 CH_2Cl_2

No. 47 $CHCl_3$

No. 48 CH_3Br

For example, the Langmuir-Blodgett method (LB method) developed by I. Langmuir's group can be used as a method for preparing a monomolecular film or a monomolecular layer built-up film of an enclosure complex, formed of a host molecule and a guest molecule, as described above. According to the LB method, for example, a monomolecular film or a monomolecular layer built-up film is prepared by utilizing the fact that, when an appropriate balance between both groups (balance of the hydrophilic group and the hydrophobic group) is maintained in a molecule whose structure comprises a hydrophilic group and a hydrophobic group therein, the hydrophilic group of the molecule faces downward on a water surface, thereby forming a

monomolecular layer. The monomolecular layer on the water surface exhibits two-dimensional characteristics. When the molecules are dispersed sparsely, a two-dimensional ideal gas equation between the surface area A and surface pressure π per molecule can be established, as shown below:

$$\pi A = kT.$$

That is, a "gas membrane" is formed. In this equation, k is Boltzmann's constant and T is absolute temperature. If A is very small, the intermolecular interaction is strong, thereby forming a two-dimensional solid "condensed film" (or solid film). A single layer of the condensed film can be transferred onto various materials (e.g., a glass plate) or onto the surface of a shaped support. The following five specific examples (methods A-E) can be used as methods of the present invention for the manufacture of a monomolecular film ("monocomplex molecular film") or a monomolecular layer built-up film of a host molecule enclosing a guest molecule, based on the solid film method described above.

(A) Host molecules and guest molecules for forming a specific enclosure complex are dissolved in a solvent, and the resulting solution is cast onto a water phase, which causes the enclosure complex to precipitate in the form of a film. In this case, if the structure of the host molecule is like that of the molecules shown in nos. 1-15, with the two terminals possessing a hydrophilic site (carboxyl group) and a hydrophobic site (alkyl group), the enclosure complex precipitated onto the water phase will spread out onto the water phase in such a manner that the hydrophilic site of the host molecule faces toward the water phase, irrespective of the hydrophilicity and hydrophobicity of

the guest molecule. On the other hand, if the structure of the host molecule is like that of the molecules shown in nos. 16-30 and the two terminals of the molecule are Z = $-CH_3$, which form a structure with only hydrophobic sites, the enclosure complex precipitated onto the water phase will spread out onto the water phase in such a manner that the hydrophilic site of the guest molecule faces toward the water phase, as shown in Figure 4. Also, if the two terminals of the host molecule are Z = -COOH, which form a structure with only hydrophilic sites, the enclosed complex formed onto the water phase will spread out onto the water phase in such a manner that the hydrophilic site of the host molecule faces toward the water phase, as shown in Figure 5.

Next, by installing a partitioning plate (or float) in such a manner that the precipitate can disperse freely but is prevented from overspreading, the spreading surface can be limited and the aggregation state of the film substance can be controlled, so that a surface pressure π proportional to the aggregation state can be achieved. A surface pressure π appropriate for the manufacture of a built-up film can be established by moving the partitioning plate, so that the spreading area can be reduced, the aggregation state of the film substance can be controlled and the surface pressure can be increased gradually. The monocomplex molecular film is transferred to a support, which is carried out by quietly moving a clean support up and down in a vertical manner, while the above-mentioned surface pressure is maintained. A monocomplex molecular film is manufactured in the manner described above. Meanwhile, in the case of the monocomplex molecular layer buildup

film, a monocomplex molecular layer buildup film with the desired degree of built-up is formed by repeating the above-mentioned operation.

Besides using the vertical immersion method for transferring a monocomplex molecular layer onto a support, other methods, such as horizontal binding methods and rotating cylinder methods, can also be used. According to the horizontal binding method, the transfer is accomplished by allowing the support to come into contact horizontally with the water surface. According to the rotating cylinder method, a monocomplex molecular layer is transferred to the support surface by rotating a cylindrical support onto the water surface. According to the above-mentioned vertical immersion method, when the support, whose surface is hydrophilic, is drawn upward from the water in a direction of cutting across the water surface, the hydrophilic group of the host molecule faces toward the support side, and a monocomplex molecular layer is formed on the support. When the support is moved upward and downward as described above, a single monocomplex molecular layer is built up each cycle. Since the direction of the film-forming molecule during the drawing-up step is different from that during the immersion step, a Y-shaped film can be formed by means of this method, wherein the hydrophilic group and the hydrophilic group of the host molecules and the hydrophobic group and the hydrophobic group of the host molecules, [respectively], between the various layers, are bound toward each other. On the other hand, according to the horizontal binding method, the transfer is accomplished by allowing the support to come into contact with the water surface horizontally, and a monocomplex molecular layer with the

hydrophobic group of the host molecule facing toward the support side is formed on the support. According to this method, even with buildup, the orientations of the film-forming molecules are not alternating, and an X-shaped film is formed, wherein the hydrophobic groups of all of the layers face toward the support side. Conversely, built-up membranes of which the hydroxy groups of all of the layers face toward the support are called Z-shaped films.

According to the rotating cylinder method, a monocomplex molecular layer is transferred to the support surface by rotating a cylindrical support onto the water surface. There is no limitation for methods of transferring a monomolecular layer onto a support. When a support with a large area is used, methods of pushing out a support from a support roller into the water phase can also be used. Additionally, the method is based on the above-mentioned principal as relating to the directions of the hydrophilic group and hydrophobic group toward the support, which can also be changed by means of treating the surface of the support or the like.

The conventional means of controlling the intrafacial orientation of the membrane substance in the above-mentioned film-forming process relies principally on controlling surface pressure. However, except in the case of the membrane substance being a compound with a considerably simple structure, such as straight-chain fatty acids, it is extremely difficult to obtain a high degree of order. On the other hand, according to the present invention, an enclosure complex is used as the film substance. Accordingly, a film with a high degree of order can be obtained in a comparatively easy manner. Specifically, as the

enclosure complex precipitates in the form of a film on a water phase, factors, such as hydrogen bonding and van der Waals forces, cause the stereoconfigurations between host and guest molecules, between host and host molecules and between guest and guest molecules to be fixed in place, so that the host molecules and guest molecules are oriented in an ordered crystalline lattice. Also, when only the guest molecule possesses a functional group, the guest molecule can be chemically modified (i.e., introduction of hydrophobic groups and hydrophilic groups), so that a decrease in functionality does not occur due to film formation.

(B) Guest molecules that exhibit water solubility are caused to dissolve in the water phase. Next, host molecules are dissolved in a solvent, and the resulting solution is cast onto the water phase. During this time, an enclosure complex between the host molecules and guest molecules forms, and the enclosure complex precipitates in the shape of a film. The combination of the host molecule and guest molecule and the film-forming process followed are conducted in accordance with the method described in (A).

(C) Guest molecules that exhibit water solubility are caused to dissolve in the water phase. Next, the host molecules and guest molecules of the targeted enclosure complex are dissolved in a solvent. The resulting solution is cast onto the water phase, and the enclosure complex precipitates in the shape of a film. The combination of the host molecule and guest molecule and the film-forming process followed are conducted in accordance with the method described in (A).

(D) Host molecules are dissolved in a solvent, and the resulting solution is cast onto the water phase. Afterward, a sealed vessel is used, and the gas-phase side thereof (i.e., the space in the vessel) is made into a guest molecule gas atmosphere. During this time, the guest molecules of the gas-phase side are enclosed, and the enclosure complex simultaneously precipitates in the shape of a film. With this method, compounds with a low boiling point that can be vaporized easily (e.g., acetone) are particularly effective for use as the guest molecule. The combination of the host molecule and guest molecule and the film-forming process followed are conducted in accordance with the method described in (A).

(E) A sealed vessel is used, and the gas-phase side thereof (i.e., the space in the vessel) is made into a guest molecule gas atmosphere. Next, the host molecules and guest molecules of the targeted enclosure complex are dissolved in a solvent. The resulting solution is cast onto the water phase, and the enclosure complex precipitates in the shape of a film. The combination of the host molecule and guest molecule and the film-forming process followed are conducted in accordance with the method described in (A).

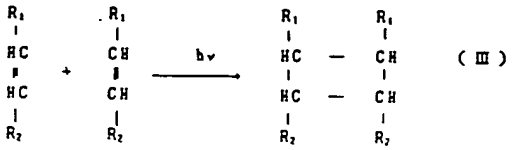
The monocomplex molecular film or monocomplex molecular layer built-up film formed onto a support in accordance with the method described above has a high density and possesses a high degree of order. By forming a recording layer with this film, a recording medium, possessing the recording functions of possible high density and high resolution (e.g., optical recording, thermal recording, electrical recording and magnetic recording),

in accordance with the function of the enclosure complex [can be produced.

When the monocomplex molecular film or monocomplex molecular layer built-up film prepared is used as a recording layer of a recording medium, various recording methods described below can be considered.

1. Optical and electrical recording media based on the dimerization of guest molecules by light or electron beam

For example, when a host molecule of any one of compound nos. 7-15 and nos. 22-30 is used in conjunction with a guest molecule possessing a photodimerizable double bond, such as compound nos. 31-38, an enclosure complex with a host molecule and guest molecule composition ratio (mole ratio) of 1:2 can be formed. When the resulting monocomplex molecular film or monocomplex molecular layer built-up film is irradiated with a light source (e.g., gamma ray, X-ray or ultraviolet light) capable of supplying sufficient energy for polymerization, in accordance with a certain pattern, a dimerization reaction occurs between the guest molecule in the irradiated area, as shown by formula III.



(III)

This reaction can be brought about when the distance between the adjacent unsaturated bonds is 4 Å or less. With the monocomplex molecular film or monocomplex molecular layer built-up film prepared in accordance with the method described above, not only can a dimer be obtained readily, the dimerization reaction generates only various possible isomers or only one kind of structural substance. Specifically, the stereoorientation of the guest molecules in the enclosure complex layer is highly ordered. Also, after dimerization, depolymerization does not occur even in a dark room, and the nonirradiated area contains the as-is monomer. Therefore, a recording in accordance with a certain pattern is formed in the manner shown in Figure 1.

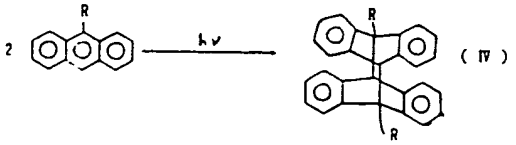
Readout of the information recorded can be conducted by means of irradiating with visible light, for example. Specifically, the conjugation system of the monomer is destroyed during the polymerization step, and as a result, the visible light absorption wavelength is altered. Since the maximum absorption wavelength shifts to the side of lower wavelength, information playback can be conducted by means of reading the changes in spectral absorption (Figure 2).

Besides reading the changes in spectral absorption with visible light, information playback can also be achieved by reading in accordance with a method of measuring the volume change before (i.e., during the monomer state) and after dimerization or in accordance with the schlieren method of measuring changes in the refractive index. These methods are particularly suitable for monocomplex molecular films or monocomplex molecular layer built-up films of a compound with a structure that exhibits a large volume change or refractive index

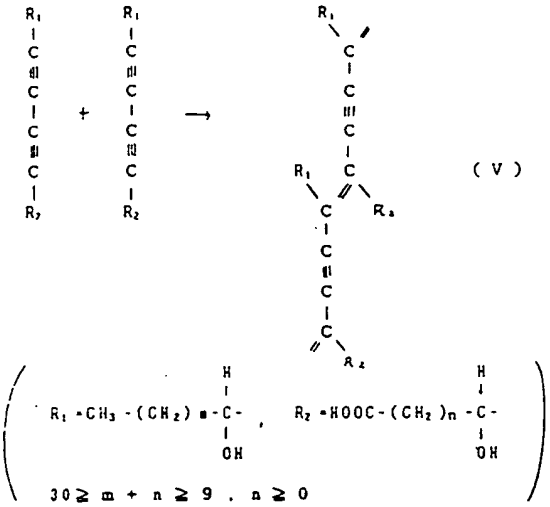
change before (i.e., during the monomer state) and after dimerization. Also, a monocomplex molecular film or monocomplex molecular layer built-up film is not formed directly on a support, but is formed on a photoconductive layer, such as Se, ZnO or CdS, formed beforehand on a support, and the difference in absorption between the monomer and the dimer is read out electrically.

When the dimer is based on a cyclobutane ring with an absorption at the wavelength of 270 nm, irradiating with ultraviolet light of a wavelength of 270 nm can convert the dimer back to the original two molecules of monomer. Accordingly, information once recorded can be erased (see Figure 3).

Additionally, compounds, such as the anthracene derivative no. 39, can also be used as photodimerizable guest molecules. In this case, the photodimerization reaction proceeds in accordance with formula IV.



Furthermore, when compound no. 7 is used as the host molecule, irradiating with light that can supply sufficient energy for polymerization (e.g., X-ray, gamma ray or ultraviolet light) can bring about polymerization between the host molecules at the irradiating area in the manner shown by formula V, which forms a polyacetylene.



Accordingly, by exposing the entire surface of a monocomplex molecular film or monocomplex molecular layer built-up film, the bonding strength between the support and the monocomplex molecular film or monocomplex molecular layer built-up film can be increased dramatically. In particular, chemical resistance (solvent resistance) can be increased. By exposing the entire surface as described above, guest molecules that exhibit photodimerization properties are also dimerized. However, when the monocomplex molecular film or monocomplex molecular layer built-up film is used as an optical recording medium, recording and display can be achieved by irradiating the medium with a light with a wavelength equivalent to the absorption wavelength of the cyclobutane ring (ultraviolet light) to bring about depolymerization, which is opposite from that of the above-mentioned examples.

It is particularly preferred that the film thickness of the above-mentioned optical recording media be 100-3000 Å.

2. Recording media which use sublimation of guest molecule

For example, [when] a host molecule of any one of compound nos. 1-30 is used in conjunction with a guest molecule of any one of compound nos. 42-48, an enclosure complex with a host molecule and guest molecule composition ratio (mole ratio) of 1:1 to 1:2 can be formed. When the resulting monocomplex molecular film or monocomplex molecular layer built-up film is irradiated with a laser or electron beam, which has sufficient energy to dissociate the guest molecules from the enclosure complex by vaporization, in accordance with a certain pattern, the guest molecules in the nonirradiated area are kept enclosed in the host molecules. Therefore, a recording in accordance with a certain pattern is formed.

When compound no. 42 is used as the guest molecule, readout of the information recorded can be conducted by means of reading the presence or absence of ultraviolet light absorption, based on the carbonyl group in this compound. Also, information playback can also be achieved by reading in accordance with a method of measuring the structural change before and after irradiating with a laser or electron beam or in accordance with the schlieren method of measuring changes in the refractive index. These methods are also effective when compound nos. 42-48 are used as the guest molecule. It is also possible that a monocomplex molecular film or a monocomplex molecular layer built-up film, containing compound no. 42 be formed on a photoconductive layer

of Se, ZnO or CdS, and then the difference in absorption between the enclosure complex area and the area of only the guest molecule is read out electrically.

It is particularly preferred that the film thickness of the above-mentioned optical recording media be 100-1000 Å.

These film-forming methods, with the principal thereof also understood, are extremely simple methods, with which recording media with excellent recording functions as described above can be offered at a low cost.

There is no limitation concerning the above-mentioned support onto which the monocomplex molecular membrane or monocomplex molecular built-up membrane of the present invention is formed. However, if a surface active substance is attached onto the support surface, the monocomplex molecular layer, when being transferred from the water surface, will be disrupted, and as a result, an excellent monocomplex molecular membrane or monocomplex molecular layer built-up membrane cannot be obtained. Accordingly, it is required that a clean support surface be used. Examples of materials that can be used as a support for the above-mentioned application include glass, metals (e.g., aluminum), plastics and ceramics.

The monocomplex molecular film or monocomplex molecular layer built-up film on the support is anchored very strongly and does not peel away from the support. Nevertheless, a bonding layer can be installed between the support and the monocomplex molecular film or monocomplex molecular layer built-up film for the purpose of enhancing the bonding strength. Additionally, the bonding strength can also be increased by means of selecting the conditions of forming the monocomplex molecular layer (e.g., the

hydrogen ion concentration in the water phase, ion species, water temperature, the speeds of raising and lowering the support, and the surface pressure).

Installing a protective film on the monomolecular film or monomolecular built-up film is desirable for improving the chemical stability of the monomolecular film or monomolecular built-up film. A protective film can either be installed or not, depending on the film-forming molecules selected.

Next, the present invention is described more specifically by means of application examples. Compound nos. 49-54 are shown in Table I.

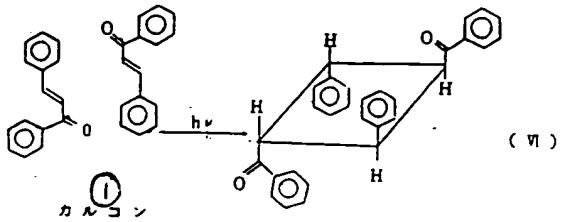
Application Example 1

An optical recording medium that involves the dimerization of the guest molecules (1)

A diacetylene diol of no. 49, which functioned as the host molecule, and chalcone, which functioned as the guest molecule, were dissolved in chloroform at a mole ratio of 1:2. The resulting solution was cast onto a water phase in which the cadmium chloride concentration was 4×10^{-4}M and the pH was 6.5. After evaporating the chloroform solvent, the surface pressure was raised to 35 dynes/cm, and an enclosure complex was caused to precipitate out in the form of a film. Afterward, the surface pressure was maintained at a constant level, while a glass plate, which was hydrophilic and had a very clean surface, was moved upward and downward quietly in a direction cutting across the

water surface at an upward/downward speed of 7 cm/min, so that the monocomplex molecular film was transferred to the support. Optical recording media, in which a monocomplex molecular film or a monocomplex molecular layer built-up film with 3, 5, 9, 15 or 19 built-up layers was used as the recording layer, were produced. During the buildup process, the support was left to stand for at least 30 min each time the support was drawn up from the water phase, and the moisture attached to the support was evaporated away. Additionally, the film-forming device employed was a Langmuir-Trough 4 made by Joyce Co (Britain).

The optical recording medium prepared was subject to X-ray irradiation in accordance with a pattern, and information pertaining to the dimerization reaction of the guest molecules, as shown by formula VI, was recorded. A high-density recording with the ordered molecules was possible.



(VI)

Key: 1 Chalcone

Information playback was conducted by reading the absorption changes in the vicinity of the wavelength 380-420 nm, which occurred accompanying the dimerization of the guest molecules. Next, depolymerization was brought about by irradiating with an ultraviolet light of a wavelength of 270 nm for 1 h, thereby erasing the recording.

Application Examples 2-12

Compound nos. 31-38 were used as the guest molecule instead of chalcone, which was used in Application Example 1. The same results were obtained. (Application Examples 2-9)

Additionally, in the case of using chalcone as the guest molecule and compound nos. 50-52 as the host molecule, recording and playback, as well as erasing the recording, can also be achieved with light, as in Application Example 1. (Application Examples 10-12)

Application Examples 13-24

An optical recording medium that involves the dimerization of the guest molecules (2)

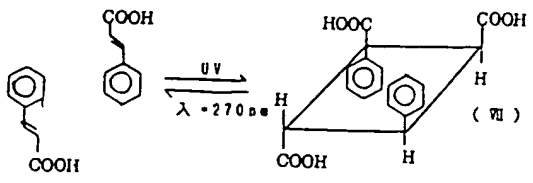
A high-pressure mercury lamp was used to subject the entire surface of each of the optical recording media described in Application Examples 1-12 to exposure, which caused all of the guest molecules to be dimerized. The resulting optical recording medium was subject, to irradiation, in accordance with a pattern, with an ultraviolet light at a wavelength of approximately 270 nm, which corresponded to the maximum absorption of the cyclobutane ring in said medium, generated in conjunction with dimerization. The action caused the guest molecules to become depolymerized, resulting in information being recorded. A recording with the ordered molecules was possible. Information playback was conducted by reading the absorption changes in the vicinity of the wavelength 380-420 nm, which occurred

accompanying the depolymerization of the guest molecules. Furthermore, the recording was erased by using a high-pressure mercury lamp to expose the entire surface of the above-mentioned recording medium. Specifically, it was confirmed that all of the guest molecules were capable of dimerizing.

Application Example 25

An optical recording medium that involves the dimerization of the guest molecules (3)

A diacetylene diol of no. 53, which functioned as a host molecule, and cinnamic acid, which functioned as a guest molecule, were used. Optical recording media, in which a monocomplex molecular film or a monocomplex molecular layer built-up film with 3, 5, 9, 15 or 19 built-up layers was used as the recording layer, were produced by means of the an same operation as that of Application Example 1. Next, a high-pressure mercury lamp was used to subject the entire surface of each of the optical recording media to exposure, which caused the guest molecules to be dimerized (formula VII) and the host molecules to be polymerized (formula V). Afterward, information was recorded by irradiating the optical recording medium with an ultraviolet light of a wavelength of 270 nm in accordance with a pattern, which caused the guest molecules to be depolymerized. A recording with the molecules was possible.



Information playback was conducted by reading the absorption changes in the vicinity of the wavelength 380-420 nm, which occurred accompanying the dimerization of the guest molecules.

Furthermore, it was confirmed that the recording can be erased by again exposing the entire surface of the above-mentioned recording medium, using a high-pressure mercury lamp. Also, the present recording medium with the entire surface thereof being exposed once to a high-pressure mercury lamp, can be used for recording/play back of information by means of the above-mentioned method, after being immersed for approximately 30 sec in alcohol, with no particular problem. Specifically, it was confirmed that the polymerization of the host molecules causes said recording medium to have a high chemical strength.

Application Examples 26 and 27

A diacetylene diol of no. 53, which functioned as a host molecule, and anthraldehyde, which functioned as a guest molecule, were dissolved in chloroform at a mole ratio of 1:2. Optical recording media, in which a monocomplex molecular film or a monocomplex molecular layer built-up film with 5, 9, 15, 31, 60 or 80 built-up layers were used as the recording layer, were produced by means of the same operation as that of Application Example 1.

Information was recorded by subjecting the prepared optical recording medium to X-ray irradiation in accordance with a pattern, which caused the guest molecules to be dimerized, as shown by formula IV. Information playback was conducted by reading the absorption changes in the vicinity of the wavelength

370-390 nm, which occurred accompanying the dimerization of the guest molecules. Next, it was confirmed that the recording can be erased by irradiating the optical recording medium with an ultraviolet light of a wavelength of 313 nm for 1 h, which brought about depolymerization.

The same results were obtained with the anthracene derivative of no. 41. (Application Example 27)

Application Example 28

A recording medium that involves the sublimation of the guest molecules (1)

A acetylene diol of no. 54, which functioned as a host molecule, was dissolved in chloroform, and the resulting solution was cast onto a water phase in which the cadmium chloride concentration was 4×10^{-4}M and the pH was 6.5. After evaporating the chloroform solvent, the gas-phase side of the system was saturated with acetone. Under an acetone atmosphere, the surface pressure was raised to 35 dynes/cm, and an enclosure complex was caused to precipitate out in the form of a film. The acetone in the gas-phase side was replaced with air or nitrogen. The surface pressure was maintained at a constant level, while a glass plate, which was hydrophilic and had a very clean surface, was moved upward and downward quietly in a direction of cutting across the water surface at an upward/downward speed of 2 cm/min, so that the monocomplex molecular film was transferred to the support. Recording media, in which a monocomplex molecular film

or a monocomplex molecular layer built-up film with 3, 5, 9, 15, 19, 40, 60 or 80 built-up layers were used as the recording layer, were produced. During the buildup process, the support was left to stand for at least 30 min each time the support was drawn up from the water phase, and the moisture attached to the support was evaporated away. Additionally, the film-forming device employed was a Langmuir-Trough 4 made by Joyce Co (Britain).

Information recording was achieved by irradiating the prepared recording medium in accordance with a pattern with a laser light, using a carbon dioxide gas laser or infrared laser, to cause the guest molecules only in the irradiated area (i.e., acetone molecules) to be sublimed away, so that the absorption (λ_{max} = 280 nm) in this area was reduced. A recording with the ordered molecules was possible. Also, recording/playback methods based on reading the presence or absence of guest molecules, using a schlieren method, can also be used. The recording could be erased and rerecording could be achieved by leaving said recording medium in an acetone gas stream for 1 h, so that acetone could be enclosed in the area in which acetone was removed. It was confirmed that the recording medium can be used repeatedly, with the above-mentioned recording/erasing/rerecording process being able to be repeated at least many tens of times.

Application Examples 29-32

When nos. 49-52 were used instead of host molecule no. 54 used in Application Example 28, results the same as those of Application Example 27 were obtained.

Application Examples 33-38

A recording medium that involves the sublimation of the guest molecules (2)

Nos. 49-52 were each used as the host molecule, and dissolved in chloroform. The resulting solution was cast onto a water phase in which the cadmium chloride concentration was 4×10^{-4}M and the pH was 6.5. During this time, the gas-phase side of the system was saturated with chloroform. Gasification of the solvent chloroform (liquid side) was allowed to occur (approximately 5 min). After the surface pressure was raised to 35 dynes/cm and an enclosure complex was caused to precipitate out in the form of a film, the chloroform in the gas-phase side was replaced with air or nitrogen. Afterward, the surface pressure was maintained at a constant level, while a glass plate, which was hydrophilic and had a very clean surface, was moved upward and downward quietly in a direction of cutting across the water surface at an upward/downward speed of 2 cm/min, so that the monocomplex molecular film was transferred to the support. Recording media, in which a monocomplex molecular film or a

monocomplex molecular layer built-up film with 3, 5, 9, 15 or 19 built-up layers was used as the recording layer, were produced.

Information recording was achieved by irradiating the prepared recording medium in accordance with a pattern with a laser light, using a carbon dioxide gas laser or infrared laser, to cause the guest molecules only in the irradiated area (i.e., chloroform) to be sublimed away. A recording with the ordered molecules was possible. Also, information playback could be achieved based on reading changes in the shape of the film that accompanied the partial removal of the guest molecules, using a schlieren method. The recording could be erased and rerecording could be achieved by leaving said recording medium in a chloroform gas stream for 1 h, so that chloroform could be enclosed. It was confirmed that the recording medium can be used repeatedly, with the above-mentioned recording/erasing/rerecording process being able to be repeated at least many tens of times.

Additionally, when benzene (no. 45; Application Example 37) or dichloromethane (no. 46; Application Example 38) was used as the guest molecule and development solvent, the same results were obtained.

Application Examples 39-44

A recording medium that involves the sublimation of the guest molecules (3)

Recording media (Application Examples 39-42), in which a monocomplex molecular film or a monocomplex molecular layer

built-up film was used as the recording layer, were produced in the same manner as in Application Example 26, using nos. 49-52 as the host molecule and 1,2-epoxypropane (no. 43) as the guest molecule. In this process, 1,2-epoxypropane (no. 43) was caused to dissolve into the water-phase side at a level of 1-10M beforehand, and the guest molecules of the gas-phase side were prevented from diffusing into the water. The methods of information recording, playback and erasing, as well as the results, were the same as those of Application Example 28.

Additionally, when acetone and ethylenimine (no. 44) were used as the guest molecule, the same results were obtained. (Application Examples 43 and 44)

Application Examples 45-48

A recording medium that involves the sublimation of the guest molecules (4)

Recording media, in which a monocomplex molecular film or a monocomplex molecular layer built-up film was used as the recording layer, were produced in the same manner as Application Example 26, using nos. 49-52 as the host molecule and methyl bromide (no. 48) as the guest molecule. The methods of information recording, playback and erasing, as well as the results, were the same as those of Application Example 28.

Application Examples 49-55

A recording medium that involves the sublimation of the guest molecules (5)

Recording media, in which a monocomplex molecular film or a monocomplex molecular layer built-up film with 3, 5 or 9 built-up layers was used as the recording layer, were produced, using no. 53 as the host molecule and nos. 42-48 as the guest molecule. The preparation method varied to some degree, depending on the type of guest molecule, and the preparation was conducted by means of the method described in Application Examples 26-44. A recording medium was produced by irradiating the entire surface of the monocomplex molecular film or the monocomplex molecular layer built-up film with a high-pressure mercury lamp to cause the host molecules to be polymerized.

The methods of information recording, playback and erasing, as well as the results, were the same as those of Application Example 26 or Application Example 28. With the present method, the bonding strength of the host molecules to the support was higher in comparison with that of Application Examples 26-44. Accordingly, it was found that the chemical strength of the recording medium was high in comparison, and that the number of repeated uses could be increased to at least 100 times.

Table I

	(1) 基本骨格	
No.49	No.10	m = 9 , n = 2
No.50	No.25	Z-COOH, n = 2
No.51	No.15	m = 9 , n = 2
No.52	No.30	Z-COOH, n = 4
No.53	No.7	m = 8 , n = 8
No.54	No.4	m = 9 , n = 2

Key: 1 Basic backbone structure

Brief explanation of the figures

Figures 1-3 are length-wise cut-away figures, describing the application examples of the image-forming medium pertaining to the present invention. Figure 1 shows the recording process; Figure 2 shows the playback process; Figure 3 shows the erasing process. Figures 4 and 5 are descriptive figures for describing the state of an enclosure complex in a water phase, pertaining to the present invention.

1	Host molecule	2	Guest molecule
3	Hydrophilic site	4	Long-chain alkyl site
5	Support	6	X-ray
7	Dimerization site	8	Visible light
9	Ultraviolet light	10, 11	Enclosure site

12, 13 Enclosed site

14 Long-chain fatty acid site

15 Hydrophobic site

16 Water phase

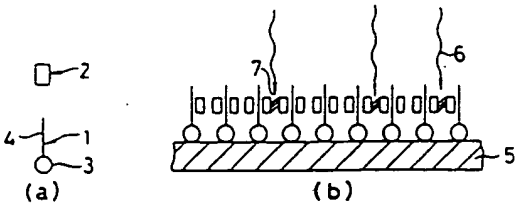


Figure 1

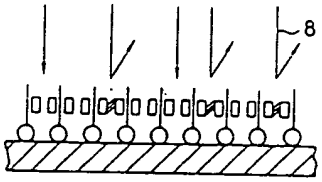


Figure 2

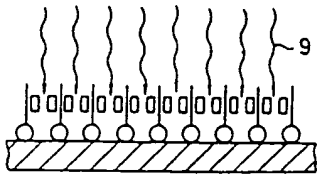


Figure 3

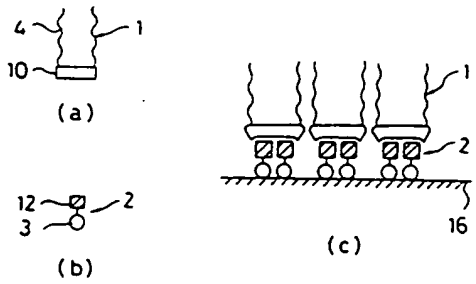


Figure 4

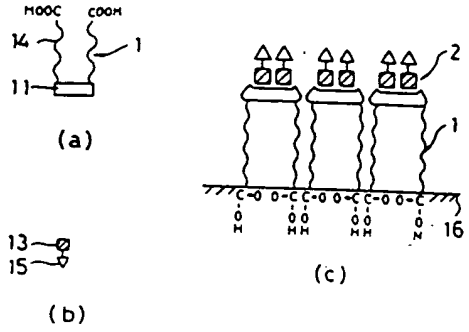


Figure 5

Best Available Copy

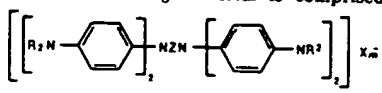
The material has good color-forming characteristics, a long shelf life, and excellent stability of the developed image dye. Thus, a color former sheet having a coated layer consisting of dispersion of 2'-anilino-3'-methyl-6'-diethylaminofluoran/2'-anilino-3'-chloro-6'-dibutylaminofluoran/gum arabic/gelatin microcapsules and an image-receiving sheet with a coating of β-hydroxyethyl 2,4-dihydroxy-6-methylbenzoate/kaolin/poly(vinyl alc.) dispersion were contacted and pressure was imagewise applied to the set. A high d. black image with excellent light stability was obtained.

104: 234358r **Microcapsules for pressure-sensitive copying paper.** Irii, Shinsuke; Tanaka, Masahito; Shiozaki, Tomoharu (Kanzaki Paper Mfg. Co., Ltd.) **Jpn. Kokai Tokkyo Koho JP 61 15,734 [86 15,734]** (Cl. B01J13/02), 23 Jan 1986, Appl. 84/137,566, 02 Jul 1984; 5 pp. Microcapsules for use in pressure-sensitive copying papers are prepd. by emulsion dispersing hydrophobic liqs. contg. $OCN(CH_2)_4CH(NCO)CO_2ZNCO$ (Z = CH_2CH_2, $CH_2CH_2CH_2$, $CHMeCH_2$) into hydrophilic liqs. and forming polymer membranes to cover the surface of the liq. drops. Thus, crystal violet lactone 2.8, benzoylleucomethylene blue 0.7, and 2,6-diisocyanatocaproic acid β-isocyanatoethyl ester 10 parts were dissolved in 100 parts K-113 (polyisopropylnaphthalene) to obtain a soln., which was then emulsified with 120 parts 1.5% aq. PVA-217 [poly(vinyl alc.)], mixed with 1.5 parts diethylenetriamine, heated to 80° for 3 h, and cooled to room temp. The resulting microcapsule dispersion was mixed with 20 parts cellulose powder and 50 parts 20% aq. oxidized starch, coated on paper (40 g/m²) at 4 g/m² (dry basis), and dried to obtain a pressure-sensitive copying paper, which showed good solvent resistance.

104: 234359s **Recording receptor and ink-jet recording method.** Toganoh, Shigeo; Arai, Ryuichi; Sakaki, Mamoru (Canon K. K.) **Ger. Offen. DE 3,510,565** (Cl. B41M5/00), 26 Sep 1985, JP Appl. 84/54,524, 23 Mar 1984; 67 pp. Ink-jet recording receptor sheets are composed of a substrate and an ink-receiving layer on which the ink can be fixed within 3 min at 20° and 65% relative humidity when the ink is applied at 0.7 mL/cm². The ink contains 30-90% water (based on the total wt. of the ink) and has a viscosity of ≤20 Cp at 25°. Thus, a transparent polyester film (100 mm), that had been hydrophilized, was coated with a compn. contg. Gohsenol KH-17 10 and water 90 parts to give a 10 mm (dry) layer. The resultant receptor material was then recorded on using an aq. ink to give a recording show an ink-fixing time, an ink point d., a suitability for overhead projection, a linear transmission factor, and a lamination suitability of 2 min, 0.8, excellent, 80%, and excellent, resp., vs. ≥1 day, 0.9, excellent, 62%, and poor, resp., for a control using a com. overhead projection film.

104: 234360k **Multistate optical switching and memory using an amphoteric organic charge transfer material.** Potember, Richard Stanley; Poehler, Theodore Otto (Johns Hopkins University) **Eur. Pat. Appl. EP 159,397** (Cl. G03C1/72), 30 Oct 1985, US Appl. 603,717, 25 Apr 1984; 55 pp. A multistate org. optical storage medium is described where an optical beam can switch any data storage spot into ≥3 memory states. The optical storage medium may consist of a mixt. of bistate switching modules, or it may consist of large delocalized amphoteric mols. The illuminated area of said optical storage medium undergoes an electrochem. topactic redox reaction which causes certain moieties in the illuminated area to change oxidn. state. By changing the intensity of the optical write beam the illuminated area can be switched to a plurality of specific states each state having a unique set of oxidn. species. An optical/spectroscopic means is used to identify the presence of oxidn. species and to read the data stored.

104: 234361m **Optical information recording medium.** Sato, Tsutomu; Umehara, Masaakira; Abe, Michiharu; Oba, Hideaki; Ueda, Yutaka (Ricoh Co., Ltd.) **Brit. UK Pat. Appl. GB 2,155,811** (Cl. G11B7/00), 02 Oct 1985, JP Appl. 84/18,222, 06 Feb 1984; 18 pp. A laser optical recording material is comprised of a plastic



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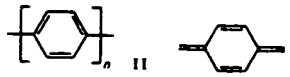
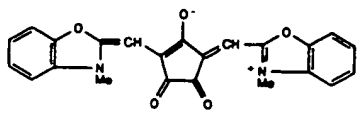


II III



IV

substrate and an org. recording layer and, optionally, an underlayer and/or a protective layer in which ≥1 of the layers contains a compd. of the formula I (R = H, lower alkyl; Z = II where n = 1, 2, III; X = acid anion; m = 0, 1, 2 being 2 when Z = II; each of the arom. rings in the compd. may be substituted with ≥1 halogen, lower alkyl, lower alkoxy, or OH). A polymethine compd. may also be contained in the recording layer as a coloring material. Thus, a 1,2-dichloroethane soln. of a 1:1 mixt. of I (R = Et; Z = phen-1,4-ylene; X^-_m = BF_4^-) and IV was spin-coated on a 1.2 mm poly(Me methacrylate) support to give a recording layer (700 Å thick). The resultant laser recording material required a writing power of 3.3 mW, had a reflectivity of 25.5%, and exhibited a C/N ratio of 52 dB vs. 3.5 mW, 20.9%, and 46 dB, resp., after light irradn. for 50 h.

104: 234362n **Image recording method.** Haruta, Masahiro; Matsuda, Hiroshi; Munakata, Hirohide; Nishimura, Yukio (Canon K. K.) **Jpn. Kokai Tokkyo Koho JP 60,192,972 [85,192,972]** (Cl. G03G17/00), 01 Oct 1985, Appl. 84/47,185, 14 Mar 1984; 8 pp.

I

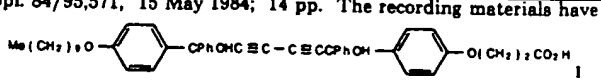
The title method consists of formation of images by reducing a metal by applying active energy signals on a recording medium having monolayers of a metal chelate on a support. The method provides high sensitivity and high-quality images. Thus, a 1 mM soln. of chelate I in $CHCl_3$ was spread on H_2O surface to form a monolayer and transferred on a SnO transparent electrode surface on a glass plate to form 3 monolayers. Another SnO_2 electrode layer on a glass plate was coated with a layer of a poly(vinylcarbazole)-trinitriofluorenone mixt. Both plates were pressed together with the coated sides in contact to obtain a recording material. Imagewise exposure of the medium to UV was carried out with the chelate layer charged pos. and the org. layer charged neg. with a 200-V elec. field. The exposed parts turned black by the Ag redn. to form a well defined image.

104: 234363p **Multicolored image recording.** Watanabe, Hideo; Hakiri, Minoru; Kubo, Keishi; Takigawa, Nobuhiro; Kawasaki, Kanjiro (Ricoh Co., Ltd.) **Ger. Offen. DE 3,514,298** (Cl. B41M5/18), 07 Nov 1985, JP Appl. 84/79,211, 19 Apr 1984; 30 pp. A method of multicolor image prodn., that gives clear multicolored images of high d. upon conventional heat-sensitive recording materials, uses a conventional heat-sensitive recording material consisting of a support and a heat-sensitive layer contg. a leuco dye and a color developer, and an image-transfer material composed of a support and ≥1 image transfer layer contg. a leuco dye selected from a yellow, magenta, or cyan leuco dye. In the recording process, the heat-sensitive color-forming layer of the thermal recording material is contacted with the image-transfer layer of the image-transfer material, and the combination selectively heated to give a multicolor image. Thus, an image-transfer material was prepd. by coating a 6 μm thick polyester film at 1 g/m² (dry) with a compn. contg. 3-diethylamino-6-chlorofluoran 15, a polyester resin 4, and MeCOEt 100 parts. A thermal recording material was then prepd. by coating a paper support at 6 g/m² (dry) with a mixt. contg. a dispersion contg. 2-(*N*-methyl-*N*-cyclohexylamino)-6-methyl-7-anilinofluoran 10, 10% aq. hydroxyethyl cellulose 10, and water 30 parts, a dispersion contg. 4,4'-isopropylidenediphenol 30, 10% aq. hydroxyethyl cellulose 30, and water 90 parts, and a dispersion contg. $CaCO_3$ 40, 10% aq. poly(vinyl alc.) 60, and water 150 parts. These two materials were then contacted layer to layer and recorded upon with a thermal heading head at 0.5 mJ to give a red image with a d. of 1.05. Upon recording at 1.0 mJ, a black image with a d. of 1.15 was obtained.

104: 234364q **Thermal printer heads.** Nagaoka, Makoto; Sugiyama, Tetsuya (Pentel Co., Ltd.) **Jpn. Kokai Tokkyo Koho JP 60,214,976 [85,214,976]** (Cl. B41J3/20), 28 Oct 1985, Appl. 84/72,412, 11 Apr 1984; 5 pp. In prepg. thermal heads for thermal printers, porous heat storage layer is formed by using a paste of glass powder, ≥20 wt.% of which is finely pulverized glass powder (av. diam. 0.5-1.0 μ). The thermal heads show improved response characteristics.

104: 234365r **Magnetic oxide magnetooptical recording material.** Koinuma, Nobuyuki; Machida, Hajime (Ricoh Co., Ltd.) **Jpn. Kokai Tokkyo Koho JP 60,220,909 [85,220,909]** (Cl. H01F1/10), 05 Nov 1985, Appl. 84/77,445, 17 Apr 1984; 6 pp. Metal oxide magnetic film for magnetooptical recording has a general formula of $Ba_{1-(x+y)}Sr_xPb_yO.n(Fe_2O_3)$ with $0 \le x \le 1$, $0 \le y \le 1$, $x + y \le 1$ and $4.5 \le n \le 6$. It contains 10-40 mol% RuO_2. The oxide may also contain a small amt. of Ga_2O_3, Al_2O_3, Cr_2O_3 and MnO. The purpose of the process is to obtain film with improved optical transmission and resistance to oxidn. corrosion. For example, $BaO.5Fe_2O_3$ + $2.2RuO_2$ sputtered on a polished quartz substrate at 500-700° had a Curie temp. of 300°, coercive force of 1.0 kOe and satn. magnetization $4\pi M_s$ of 2.4 kG.

104: 234366s **Information recording materials.** Matsuda, Hiroshi; Haruta, Masahiro; Hirai, Yutaka; Nishimura, Yukio; Eguchi, Takeshi; Nakagiri, Takashi (Canon K. K.) **Jpn. Kokai Tokkyo Koho JP 60,239,739 [85,239,739]** (Cl. G03C1/72), 28 Nov 1985, Appl. 84/95,571, 15 May 1984; 14 pp. The recording materials have



I

a recording layer composed of a monolayer or superposed monolayers of inclusion compds. consisting of host mols. having hydrophilic portion, hydrophobic portion, and portion for inclusion, and the included guest mols. Information is recorded by inducing chem. or phys. changes of the layer by irradn. This enables high d., erasable, and rewritable recordings. Dimerization, evapn., and sublimation of guest mols. are utilized as the means of recording. Thus, a 1:2 mixt. of I (host) and [redacted] guest) in $CHCl_3$ was spread on the surface of a soln. of 0.4 mM $CdCl_2$ (pH 4.5) and evapd. After compression, the film was transferred onto a glass support, up to 19 monolayers, to obtain a recording material. Patternwise irradn. with x-ray made high d. recording. Absorption change in the region 380-420 nm was induced by dimerization of chalcone. UV irradn. for 1 h erased the recording, by reverse reaction.

⑲日本国特許庁(JP)　⑪特許出願公開

⑫公開特許公報(A)　昭60-239739

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B 41 M 5/26		7447-2H	
G 11 B 7/24		A-8421-5D	審査請求　未請求　発明の数 1　(全14頁)

⑤4発明の名称　記録媒体

⑳特　願　昭59-95571
㉒出　願　昭59(1984)5月15日

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明細書

1.発明の名称

記録媒体

2.特許請求の範囲

その分子内に親水性部位、疎水性部位及び包接部位を有するホスト分子と該ホスト分子に包接されるゲスト分子とからなる包接錯体の単分子膜又は単分子層累積膜を担体上に形成して記録層としたことを特徴とする記録媒体。

3.発明の詳細な説明

(1) 技術分野

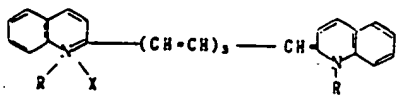
本発明は、包接錯体の単分子膜、乃至単分子層累積膜の化学変化若しくは物理変化を利用して記録を行なう記録媒体に関する。

(2) 背景技術

従来、有機化合物を記録層とする記録媒体としては種々のものが知られている。

例えば、有機化合物を薄膜にして記録層として用いる光記録媒体については、例えば特開昭56-16948号公報、特開昭58-125246号公報にも開示されている。いずれも有機色素を記録層とし、レーザビームにより記録再生を行なうレーザ記録媒体に関するものである。特に、特開昭58-125246号公報に開示された媒体は、

一般式(I)



(I)

で表わされるシアニン系色素の薄膜を記録層とするものである。(I)式で表わされるシアニン系色素溶液を回転塗布機などを用いて、1000Å以下の厚さ、例えば約300Åの厚さにプラスチック基板上に塗布し薄膜を形成する。膜内の分子分布配向がランダムであると、光照射に伴って膜内で光の散乱が生じ、微視的にみた場合各光照射の度に生ずる化学反応の度合が異なってくる。そこで記録媒体としては、膜内の分子分布、配向が一様になっていることが望ましく、またできる限り膜厚が薄いことが、記録の高密度化のために要請される。しかしながら、塗布法による場合、膜厚にお

いては 300Å程度が限界であり、膜内の分子分布、配向がランダムであることは解決しがたいことであった。

レジスト材料の一つとして光量子効率が大でかつ優れた解像力を有するものとして提案されていたジアセチレン化合物累積膜が、レジスト材料のみならず、薄膜電気－光学デバイス、電気－音響デバイス、圧・焦電デバイス等にも応用されることが、特開昭56-42229号公報、特開昭56-43220号公報などに示されている。

近時においては、ジアセチレン化合物累積膜の製造方法の改良について特開昭58-111029号公報に示されている。かかる発明にて製造された基板上のジアセチレン化合物累積膜は紫外線を照射することにより重合させてジアセチレン化合物重合体膜を作り、或はマスキングして紫外線を照射し部分的に重合させ、未重合部分を除去して図形を作り、薄膜光学デバイスや集積回路素子として使用される。

しかし、これらはいずれもジアセチレン化合物に限るものであり、薄膜光学デバイスとして使用するときに、一度記録したものの消去の可能性については述べられていない。

一方、上述欠点を解決すべく、分子内に親水基、疎水基及び少なくとも1個の不飽和結合を有する1種類の光重合性モノマーの単分子膜又は単分子層累積膜を基板上に形成して記録層としたことを特徴とする、反復使用可能な光記録媒体が特願昭58-190932号の光記録媒体に示されている。

これらのジアセチレン化合物累積膜にしても、光重合性オレフィンモノマーの単分子膜若しくは単分子層累積膜にしても、光反応性化合物に親水基、疎水基を導入して、直接基板上に担持させる製法を採用している。従って、種々の機能性膜を簡単に作製することが困難なのに加えて、親水基、疎水基の導入に伴う光反応性の低下の恐れがあった。更には、非常に高度な高密度記録を行う際に重要となる、膜面内の分子配向の制御についても、極めて複雑な操作が要求される問題があった。

かかる従来例の欠点を解消し、1)各種の機能性膜を比較的簡単に作製する方法、2)その際、機能性分子の持つる種機能が、薄膜化した場合においても、損失若しくは低下されることなく発現するほに膜化する方法、更には、3)上記の薄膜化において、特別な操作を行うことなしに、膜構成分子が膜面内方向に対して、高度の秩序構造を持って配向される方法を種々検討した結果、本発明を成すに至った。又、かかる成膜法を用いて、高感度、高解像度の記録媒体を、容易にかつ高品質に提供できるに至った。

(3) 発明の開示

本発明の目的は、外因により分子単位での化学変化若しくは物理変化を起こす様な高密度記録媒体を提供することにある。

また、この様な分子単位での高密度記録を行うのに際して重要な因子となる媒体面内での分子配向に関して、従来例よりも秀逸な媒体を提供することにある。更には、上述記録媒体を製造するに当って、比較的簡単な操作変更により、種々な性質を有する媒体を提供することにある。

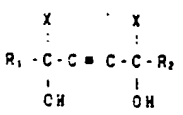
本発明の上記目的は、以下の本発明によって達成される。

その分子内に親水性部位、疎水性部位及び他分子との包接が可能な部位（包接部位）を有する分子（ホスト分子）と該ホスト分子に包接される別種の分子（ゲスト分子）とからなる包接錯体の単分子膜又は単分子層累積膜を担体上に形成して記録層としたことを特徴とする記録媒体。

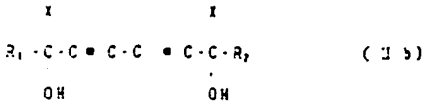
本発明の記録層を構成する物質は、分子内に親水性部位、疎水性部位及び他分子との包接が可能な部位を少なくとも1ヶ所有する分子（これをホスト分子と呼ぶ）と該ホスト分子に包接される別種の分子（これをゲスト分子と呼ぶ）の二種の分子からなる。かかるホスト分子とゲスト分子とからなる包接錯体の単分子膜、乃至単分子層累積膜を担体上に形成することにより、本発明の記録媒体が形成される。但し、これら二種類の分子の内、どちらか一方、若しくは、両方が、光、熱、電気、磁気等の外因により、化学変化若しくは物理

変化を起こすことが必要である。即ち、本発明における記録媒体は、前述の化学変化や物理変化を利用して記録を行なう。

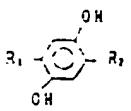
本発明に用いられるホスト分子としては、上述の如く、分子内の適当な位置に親水性部位、疎水性部位及び少なくとも1ヶ所の他種分子との包接錯体を形成可能な部位を有する分子であれば広く使用することができる。分子内に親水性部位や疎水性部位を形成し得る構成要素としては、一般に広く知られている各種の親水基や疎水基等が代表的なものとして挙げられる。他種分子との包接錯体を形成し得る部位は、水酸基、カルボニル基、カルボキシル基、エステル基、アミノ基、ニトリル基、チオアルコール基、イミノ基等の導入によって形成される。このようなホスト分子を、一般式(IIa)～(IIc)で示される水酸基を持つホスト分子を例として、以下に具体的に説明する。



(IIa)



(IIb)



(IIc)

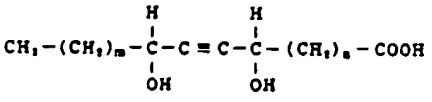
(ここで、X=H または C_6H_5 である。)

すなわち、分子内に親水性部位および疎水性部位を有するとは、例えば上式においてR₁部及びR₂部の何れか一方に親水性部位が存在し、他方に疎水性部位が存在するか、R₁部及びR₂部が両部以外の残りの部との関係において共に親水性、若しくは疎水性を示すことを言う。R₁部及び、R₂部の構造に関して、疎水性部位を導入する場合には特に炭素原子数5～30の長鎖アルキル基が、又親水性部位を導入する場合には特に炭素原子数1～30の脂肪酸が望ましい。

本発明におけるホスト分子を更に具体的に示せば、例えば以下に列挙するアセチレンジオール誘導体(No.1～No.6, No.16～No.21)、ジアセチレンジオール誘導体(No.7～No.12, No.22～No.27)、ハイドロキノン誘導体(No.13～No.15, No.28～No.30)等が利用し得るものとして挙げられる。尚、以下の例における m, n は、正の整数を、Zは、$-CH_3$ または $-COOH$ を、Phは、$-C_6H_5$ を示すものとする。

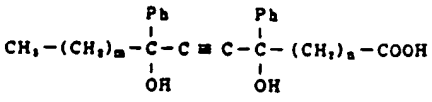
(アセチレンジオール誘導体の例)

No. 1



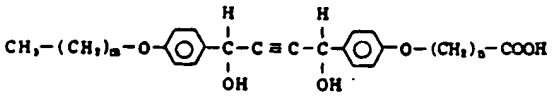
$30 \geq m+n \geq 11,\ n \geq 0$

No. 2



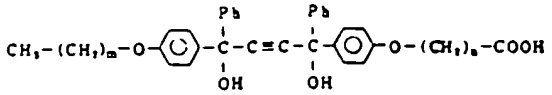
$30 \geq m+n \geq 11,\ n \geq 0$

No. 3



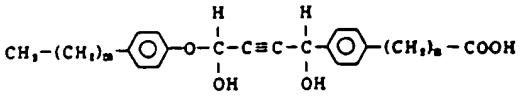
$30 \geq m+n \geq 8,\ n \geq 1$

No. 4



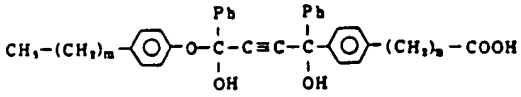
30 ≧ m + n ≧ 8, n ≧ 1

No. 5



30 ≧ m + n ≧ 8, n ≧ 0

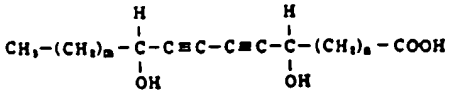
No. 6



30 ≧ m + n ≧ 8, n ≧ 0

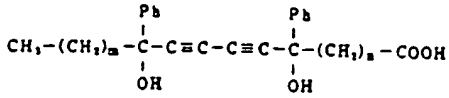
〔ジアセチレンジオール誘導体の例〕

No. 7



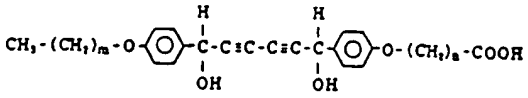
30 ≧ m + n ≧ 9, n ≧ 0

No. 8



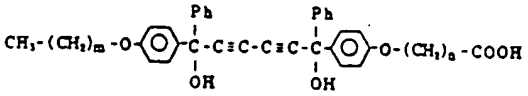
30 ≧ m + n ≧ 9, n ≧ 0

No. 9



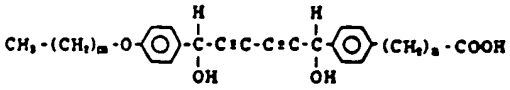
30 ≧ m + n ≧ 5, n ≧ 1

No. 10



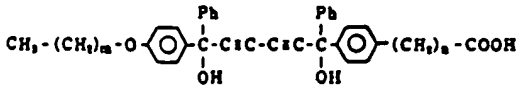
30 ≧ m + n ≧ 5, n ≧ 1

No. 11



30 ≧ m + n ≧ 5, n ≧ 0

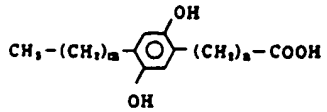
No. 12



30 ≧ m + n ≧ 5, n ≧ 0

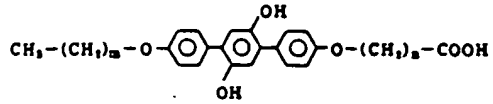
〔ハイドロキノン誘導体の例〕

No. 13



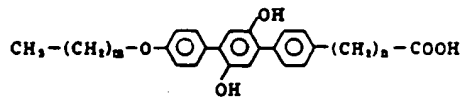
30 ≧ m + n ≧ 13, n ≧ 0

No. 14



30 ≧ m + n ≧ 9, n ≧ 1

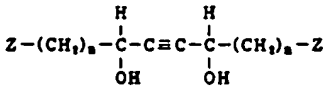
No. 15



30 ≧ m + n ≧ 9, n ≧ 0

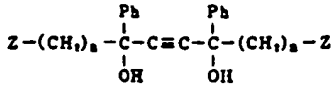
〔アセチレンジオール誘導体の例〕

No. 16



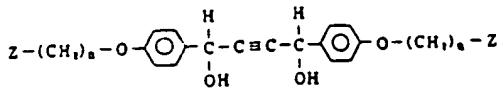
30 ≧ n ≧ 5

No. 17



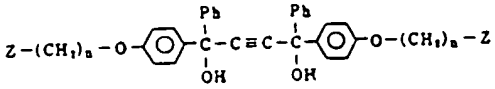
30 ≧ n ≧ 5

No. 18



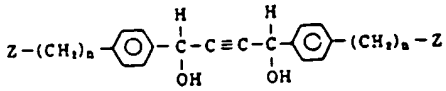
30 ≧ n ≧ 4

No. 19



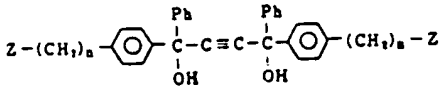
30 ≧ n ≧ 4

No. 20



30 ≧ n ≧ 4

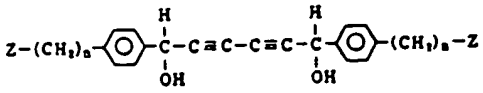
No. 21



30 ≧ n ≧ 4

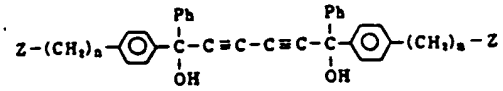
30 ≧ n ≧ 1

No. 26



30 ≧ n ≧ 1

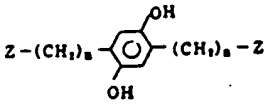
No. 27



30 ≧ n ≧ 1

（ハイドロキノン誘導体の例）

No. 28

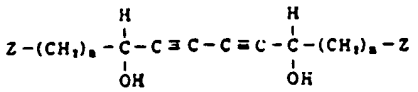


30 ≧ n ≧ 5

No. 29

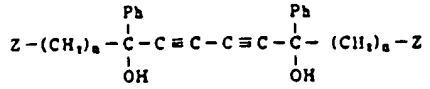
（ジアセチレンジオール誘導体の例）

No. 22



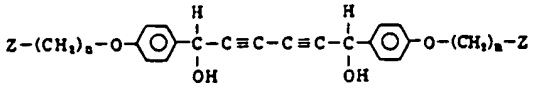
30 ≧ n ≧ 3

No. 23



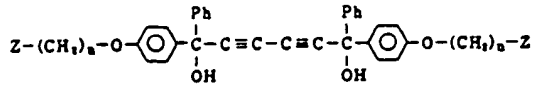
30 ≧ n ≧ 3

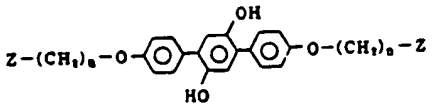
No. 24



30 ≧ n ≧ 1

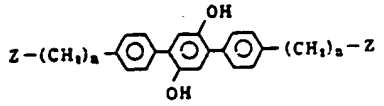
No. 25





30 ≧ n ≧ 1

No. 30



30 ≧ n ≧ 1

上に挙げた化合物はホスト分子に長鎖アルキル基や長鎖カルボン酸等を置換させて親水性や疎水性を導入した点を除けばそれ自体既知の化合物であり、又、長鎖アルキル基等で修飾されていないホスト分子が、種々のゲスト分子と結晶性の包接錯体を形成する点に関しても、日本化学会誌No.2 239頁-242頁（1983年）に述べられている。

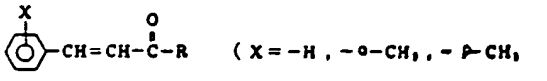
これらホスト分子と包接錯体を作り得るゲスト分子としては、一般に、ホスト分子と強い水素結合を形成し得る分子が望ましい。従って、先に述べた如く、ホスト分子が包接部位として水酸基を有する場合には、ゲスト分子として、アルデヒド、ケトン、アミン、スルフォキシド等を挙げることができる。また、ゲスト分子としては他に、各種ハロゲン化合物、或いはπ-電子系化合物、即ちアルケン、アルキン、及びアレーン等を選ぶ事もできる。何れにせよ、形成される包接錯体が所望の記録機能を示す構造を有する分子が選ばれる。

以下、各種機能別に利用可能なゲスト分子の具体例を示す。

(1) ゲスト分子の二量化反応を用いた光記録媒体に利用し得るゲスト分子の具体例としては、オレフィン化合物（No.31 ～No.34）、ジオレフィン化合物（No.35 ～No.38）、アントラセン誘導体（No.39）、2-アミノピリジニウム（No.41）等。

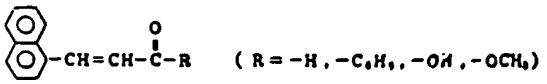
（オレフィン化合物の例）

No. 31



（X＝-H，-o-CH_3，-p-CH_3
R＝-H，-C_2H_5，-OH，-OCH_3）

No. 32



（R＝-H，-C_2H_5，-OH，-OCH_3）

No. 33

No. 34

（$R_1=R_2=CH_3$ または $R_1=CH_3$、$R_2=H$）

（ジオレフィン化合物の例）

No. 35

（Ar＝ の場合は、Ar'＝ ， ，
Ar＝ の場合は、Ar'＝ ， ，
， ）

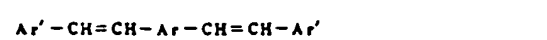
No. 36

（Ar＝ の場合は、R＝HO-，CH_3O-，
C_2H_5O-， -O-，NH_2-，O_2N- ，
Ar＝ の場合は、R＝CH_3O-）

No. 37

（R=-$COOCH_3$，-$COOC_2H_5$）

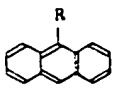
No. 38



（R＝C_6H_5-，-$COOCH_3$）

〔アントラセン誘導体の例〕

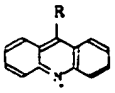
No. 39



（R = CH_3-, CHO-, -$COOC_2H_5$, Br-）

〔アクリジニウム誘導体の例〕

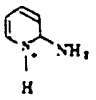
No. 40



・X^-　（R = -H, -CH_3, -C_2H_5,
X^- = I^-, Br^-, Cl^-）

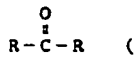
〔2－アミノピリジニウム〕

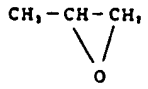
No. 41

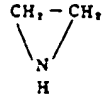


・X^-　（X^- = Cl^-, Br^-, I^-）

(2) ゲスト分子の昇華を利用した記録媒体に利用し得るゲスト分子の具体例としては、ケトン（No. 42）、1，2－エポキシプロパンなどのエポキシド（No. 43）、エチレンイミン（No. 44）、ベンゼン（No. 45）、ジクロルメタン，クロロホルムなどの塩化物（No. 46，No. 47）、臭化メチルなどの臭化物（No. 48）等、

No. 42　  　（R = -CH_3, -C_2H_5）

No. 43　 

No. 44　 

No. 45　

No. 46　CH_2Cl_2

No. 47　$CHCl_3$

No. 48　CH_3Br

が挙げられる。

このようなホスト分子およびゲスト分子から成る包接錯体の単分子膜または単分子層累積膜を作成する方法としては、例えばI.Langmuirらの開発したラングミュア・ブロジェット法（LB法）を用いる。LB法は、例えば分子内に親水基と疎水基を有する構造の分子において、両者のバランス（両親媒性のバランス）が適度に保たれているとき、分子は水面上で親水基を下に向けて単分子の層になることを利用して単分子膜または単分子層の累積膜を作成する方法である。水面上の単分子層は二次元系の特徴をもつ。分子がまばらに散開しているときは、一分子当り面積Aと表面圧Πとの間に二次元理想気体の式、

$$\Pi A = kT$$

が成り立ち、"気体膜"となる。ここに、kはボルツマン定数、Tは絶対温度である。Aを十分小さくすれば分子間相互作用が強まり二次元固体の"凝縮膜（または固体膜）"になる。累積膜はガラス基板などの種々の材質や形状を有する固体の表面へ一層ずつ移すことができる。この方法を用いて、本発明のゲスト分子を包接するホスト分子の単分子膜（これを単錯体分子膜と呼ぶことにする）、若しくは単錯体分子層累積膜の具体的な製法としては、例えば以下に示すA～Eの5法を挙げることができる。

［A］目的とする包接錯体のホスト分子とゲスト分子とを溶剤に溶解し、これを水相上に展開させて包接錯体を膜状に析出させる。この場合、ホスト分子の構造がNo.1-No.15に示したような分子の両端に親水性部位（カルボキシル基）と疎水性部位（アルキル基）を併有するものであれば、水相上に析出する包接錯体はゲスト分子の親水性および疎水性のいかんにかかわらず、ホスト分子の親水性部位を水相に向けた状態で水相上に展開する。一方、ホスト分子がNo.16 - No.30 に示した構造をとる場合、分子の両端が疎水性部位のみで構成される Z-CH_3 は、水相上に析出する包接錯体は、ゲスト分子の親水性部位を水相に向けた第4図に示すような状態で水相上に展開する。又、分子の両端が親水性部位のみで構成される

2-COOH では水相上に形成される包接錯体は、ホスト分子の親水性部位を水相に向けた第5図にホすような状態で水相上に展開する。

次にこの析出物が水相上を自由に拡散して広がりすぎないように仕切板（ムたは浮子）を設けて展開面積を制限して被物質の集合状態を制御し、その集合状態に比例した表面圧Πを得る。この仕切板を動かし、展開面積を縮少して被物質の集合状態を制御し、表面圧を徐々に上昇させ、累積膜の製造に適する表面圧Πを設定することができる。この表面圧を維持しながら静かに清浄な担体を垂直に上下させることにより単錯体分子膜が担体上に移しとられる。単錯体分子膜は以上で製造されるが、単錯体分子層累積膜は前記の操作を繰り返すことにより所望の累積度の単錯体分子層累積膜が形成される。

単錯体分子層を担体上に移すには、上述した垂直浸せき法の他、水平付着法、回転円筒法などの方法による。水平付着法は担体を水面に水平に接触させて移しとる方法で、回転円筒法は、円筒型の担体を水面上を回転させて単錯体分子層を担体表面に移しとる方法である。前述した垂直浸せき法では、表面が親水性である担体を水面を横切る方向に水中から引き上げるとホスト分子の親水基が担体側に向いた単錯体分子層が担体上に形成される。前述のように担体を上下させると、各行程ごとに1枚ずつ単錯体分子層が積み重なっていく。成膜分子の向きが引上げ行程と浸せき行程で逆になるので、この方法によると各層間はホスト分子の親水基と親水基、ホスト分子の疎水基と疎水基が向かい合うY型膜が形成される。それに対し、水平付着法は、担体を水面に水平に接触させて移しとる方法で、ホスト分子の疎水基が担体側に向いた単錯体分子層が担体上に形成される。この方法では、累積しても、成膜分子の向きの交代はなく全ての層において、疎水基が担体側に向いたX型膜が形成される。反対に全ての層において親水基が担体側に向いた累積膜はZ型膜と呼ばれる。

回転円筒法は、円筒型の担体を水面上を回転させて単分子層を担体表面に移しとる方法である。単分子層を担体上に移す方法は、これらに限定されるわけではなく、大面積担体を用いる時には、担体ロールから水相中に担体を押し出していく方法などもとり得る。また、前述した親水基、疎水基の担体への向きは原則であり、担体の表面処理等によって変えることもできる。

以上の成膜過程に於いて被物質の面内方向の配向性制御は従来、主として表面圧の制御に依って成されていた訳であるが、被物質が余程単純な構造の化合物、例えば直鎖脂肪酸等の場合を除き、高い秩序性を得ることは極めて困難であった。然るに本発明に於いては、包接錯体を被物質に用いるので、高い秩序性を持つ膜を比較的簡単に得ることができる。即ち、水相上に包接錯体が膜状に析出した時点で、水素結合やファン・デル・ワールス力等に因ってホスト分子－ゲスト分子間、ホスト分子－ホスト分子間、ゲスト分子－ゲスト分子間の立体的配置は固定され、各ホスト分子及びゲスト分子は結晶格子的秩序性を持って配列する。又、ゲスト分子のみが機能性を持つ場合には、このゲスト分子への化学的修飾、即ち、疎水基や親水基の導入を行わないので、膜化に伴う機能の低下は生じない。

〔B〕水溶性を示すゲスト分子を水相に溶解させる。次にホスト分子を溶剤に溶解せしめてこれを水相上に展開させる。この時同時にホスト分子－ゲスト分子間で包接錯体形成が行われて膜状に析出する。ホスト分子とゲスト分子の組み合わせ及び以下の成膜操作については〔A〕に示した方法に準ずる。

〔C〕水溶性を示すゲスト分子を水相に溶解させる。次に、目的とする包接錯体のホスト分子とゲスト分子とを溶剤に溶解し、これを水相上に展開させて包接錯体を膜状に析出させる。ホスト分子とゲスト分子の組み合わせ及び以下の成膜操作については〔A〕に示した方法に準ずる。

〔D〕ホスト分子を溶剤に溶解しこれを水相中に展開させる。その後、密閉系の装置を用いて気相側、即ち装置内の空間をゲスト分子ガス雰囲気と

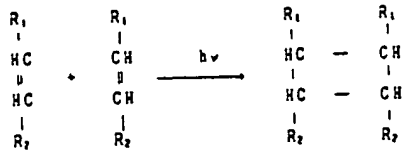
する。この時、同時に気相側のゲスト分子を包接し、包接錯体が結晶状に析出する。この方法はゲスト分子が低沸点で気化し易い性質を持つ化合物、例えばアセトン等の場合、特に有効である。ホスト分子とゲスト分子の組み合わせ及び以下の成膜操作については〔A〕に示した方法に準ずる。

〔E〕密閉系の装置を用いて気相側、即ち装置内の空間をゲスト分子ガス雰囲気とする。次に目的とする包接錯体のホスト分子とゲスト分子とを溶剤に溶解し、これを水相上に展開させて包接錯体を結晶状に析出させる。ホスト分子とゲスト分子の組み合わせ及び以下の成膜操作については、〔A〕に示した方法に準ずる。

上述の方法によって担体上に形成される単錯体分子膜及び単錯体分子層累積膜は高密度でしかも高度の秩序性を有しており、これらの膜で記録層を構成することによって、包接錯体の機能に応じて光記録、熱的記録、電気的記録あるいは磁気的記録等の可能な高密度で高解像度の記録機能を有する記録媒体を得ることができる。

ゆえした単錯体分子膜及び単錯体分子層累積膜を記録媒体の記録層として用いる場合以下に示すほにる種の記録法が考えられる。

1.ゲスト分子の光又は電子線二量化反応を用いた光又は電子線記録媒体例えばホスト分子に No.7～15、No.22～30の何れかと、No.31-38等の光二量性二重結合を有するゲスト分子とを組み合わせるとホスト分子対ゲスト分子の組成比（mol比）が1：2の包接錯体が形成される。この単錯体分子膜、若しくは、単錯体分子層累積膜にあるパターンに従ってガンマ線、X線、紫外線など重合に必要なエネルギーを供給しうる光を照射すると照射部位において㈢式に示すようにゲスト分子間で二量化反応がおこる。



（㈢）

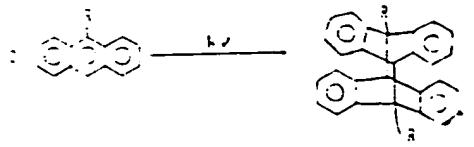
これらの反応は互いに隣接する不飽和結合の距離が4Å以下のときおこり得るものであるが、先に述べたほな方法で作成された単錯体分子膜又は、単錯体分子層累積膜では、二量化物が容易に得られるのみならず、二量化反応に伴って生成が考えられる種の異性体若しくは構造体の唯一種しか生成されない。即ち、包接錯体層に於けるゲスト分子間の立体配列は、極めて整然としている。また、二量化した後は、常所下でも解重合は起らず、非照射部位は単量体のままであるので、第1図に示すように、或るパターンに従った記録が成される。

記録された情報の読み取りは例えば可視光の照射によって行なう。すなわち、重合によって単量体時の共役系が崩れるので、可視光の吸収波長に変化をきたす。最大吸収波長は低波長側にシフトするので、吸収スペクトル変化を読みとることにより情報の再生が行なわれる（第2図）。

再生は、可視光による吸収スペクトル変化の読み取り以外にも、単量体時と二量化後の体積変化又は屈折率変化をシュリーレン法により読みとることも可能である。この方法は、単量体時と二量化後の体積変化又は屈折率変化の大きい構造を有する化合物の単錯体分子膜または単錯体分子層累積膜のときには特に適している。また、単錯体分子膜または単錯体分子層累積膜を基板の上に直接ではなく、基板上にSe、ZnO、CdSなどの光導電体層を形成し、その上に単錯体分子膜または単錯体分子層累積膜を形成することにより、単量体と二量体の吸光度の差を電気的に読み取ることも可能である。

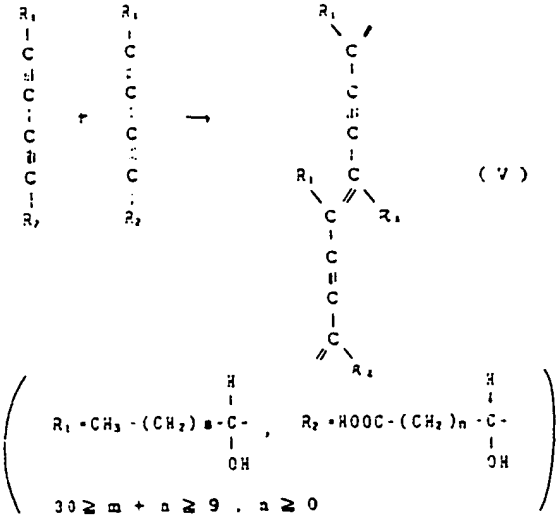
二量体はシクロブタン環に基づく、波長270nmの吸収を持つが、この波長270nmの紫外光を照射することによって二量体は元の単量体二分子に戻る。従って一度記録された情報の除去が可能となる。（第3図）

なお光二量性のゲスト分子としてアントラセン誘導体 No.39の如き化合物を用いる事もできる。この場合光二量化反応は㈣式に従って進行する。



（ヲ）

又、ホスト分子としてNo.7を用いた場合には、X線、ガンマ線、紫外線等の場合に必要なエネルギーを供給し得る光を照射すると、照射部位に於いてV式に示す様にホスト分子間で重合がおこり、ポリジアセチレンが形成される。



（V）

従って、単結晶分子膜若しくは単結晶分子層累積膜に全面露光することにより、基板との付着力を飛躍的に増大せしめることが可能である。特に耐薬品（耐溶剤）性が増大する。かかる、全面露光により、ゲスト分子が光二量性を示す場合にはゲスト分子も、二量化してしまうが、これを光記録媒体として用いる際には、前述例とは逆にパターンに従ってシクロブタン環の吸収波長に等しい波長の光（紫外光）を照射して解重合させることにより記録乃至表示が出来る訳である。

以上述べた光記録媒体に於いて膜厚は、特に100～3000Åのものが好ましい。

2.ゲスト分子の昇華を利用した記録媒体

例えばホスト分子としてNo.1～30の何れかと、No.42－48等のゲスト分子を組合わせると、ホスト分子対ゲスト分子の組成比（mol比）が1：1乃至1：2の包接結晶体が形成される。この単結晶分子膜若しくは単結晶分子層累積膜にあるパターンに従ってこれらゲスト分子が包接結晶体より解離して気化するに十分なエネルギーを有するレーザ光や電子線等を照射すると非照射部位に於いては、ゲスト分子はホスト分子に包接されたままであるので上記パターンに従った記録が成されたことになる。

記録された情報の読み取りは、ゲスト分子としてNo.42、を用いた場合にはこれらの化合物が持つカルボニル基に基づく紫外光吸収の有無を読みとることにより成される。又、レーザ光や電子線照射前後の膜の構造変化又は屈折率変化をシュリーレン法により読み取ることもでき、この方法は、ゲスト分子としてNo.42～48を用いた場合にも有効である。又、No.42を含む単結晶分子膜乃至単結晶分子層累積膜をSe、ZnO、CdS等の光導電体層上に形成することにより包接結晶体部とゲスト分子のみの部位との吸光度の差を電気的に読み取ることも可能である。

以上の記録媒体に於いて膜厚は、特に100～1000Åのものが好ましい。

これら成膜方法はその原理からも分る通り、非常に簡易な方法であり、上記のような優れた記録

積膜を有する記録媒体を低コストで提供することができる。

以上述べた、本発明における単結晶分子膜または単結晶分子累積膜を形成する担体は特に限定されないが、担体表面に界面活性物質が付着していると、単結晶分子層を水面から移しとる時に、単結晶分子膜が乱れ良好な単結晶分子膜または単結晶分子層累積膜ができないので担体表面が清浄なものを使用する必要がある。使用することのできる担体の例としては、ガラス、アルミニウムなどの金属、プラスチック、セラミックなどが挙げられる。

担体上の単結晶分子膜または単結晶分子層累積膜は、十分に強く固定されており担体からの剥離、剥落を生じることはほとんどないが、付着力を強化する目的で担体と単結晶分子膜または単結晶分子層累積膜の間に接着層を設けることもできる。さらに単結晶分子層形成条件例えば水相の水素イオン濃度、イオン場、水温、担体上げ下げ速度あるいは表面圧の選択等によって付着力を強化することもできる。

単分子膜または単分子層累積膜の上に保護膜を設けることは、単分子膜または単分子層累積膜の化学的安定性を向上させるためには、好ましいことであるが、実験分子の選択によって保護膜は設けても設けなくてもよい。

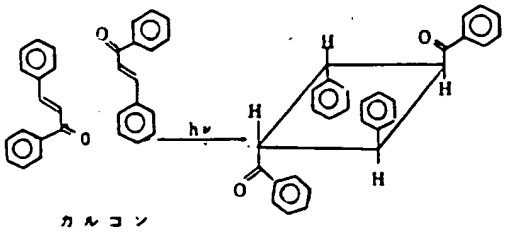
以下に本発明の実施例を示して更に具体的に説明する。 No.49～ No.54の化合物は、第1表に示す。

実施例 1

ゲスト分子の光二量化反応を用いた光記録媒体（1）

ホスト分子として No.49のジアセチレンジオールと、ゲスト分子としてカルコンをモル比1：2の割合でクロロホルムに溶かした後、pH6.5、塩化カドミウム濃度 4×10^{-4} Mの水相上に展開させた。溶媒のクロロホルムを蒸発除去後、表面圧を35dynes/cmまで高めて、包接錯体を膜状に析出させた。この後、表面圧を一定に保ちながら、表面が十分に清浄で親水性となっているガラス基板を上下速度7cm/minにて水面を横切る方向に静かに上下させ、単結晶分子膜を基板上に移し取り、単結晶分子膜及び3，5，9，15，19層に累積した単結晶分子層累積膜を記録層とする光記録媒体を製造した。この累積行程において基板を水相から引きあげる際に、30分間以上放置して、基板に付着している水分を蒸発除去した。なお成膜装置としては、英国 Joyce社製の Langmuir-Trough4を使用した。

作成した光記録媒体にパターンに従って、X線照射を行い、式(1)に示すゲスト分子の二量化反応を行ない情報を記録した。分子オーダーの高密度記録が可能であった。



カルコン　　(1)

記録の再生はゲスト分子の二量化に伴う波長380nm～ 420nm付近の吸収変化を読み取る事により行った。次いで波長 270 nm の紫外光を1時間照射したところ、脱重合がおこり、記録が消去がされた。

実施例 2～17

実施例1のカルコンの代わりにゲスト分子として No.31～ No.38の化合物を用いた場合も同様の結果を得た。（実施例 2～9）

又、ゲスト分子をカルコンとし、ホスト分子を No.50～ No.52とした場合にも、実施例1と同様、光に依る記録、再生、更には、記録の消去が可能であった。（実施例10～12）

実施例13～24

ゲスト分子の光二量化反応を用いた光記録媒体(2)

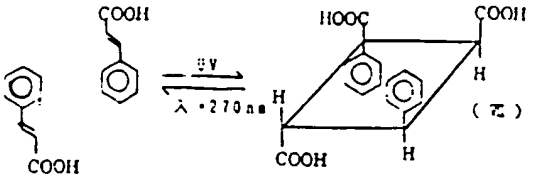
実施例1～12で造べた各光記録媒体を先づ高圧水銀灯により全面露光せしめて、全てのゲスト分子を二量化した。かかる媒体に二量化に伴って生成されたシクロブタン環の吸収極大に相当する波

長270nm 付近の紫外光をパターン状に照射し、ゲスト分子を解重合し情報を記録した。分子オーダーの記録が可能であった。記録の再生は、ゲスト分子の解重合に伴う波長 380～420nm 付近の吸収変化を読み取る事により行った。更に再び高圧水銀灯を用いて上記記録媒体を全面露光することにより、記録を消去、即ち、全てのゲスト分子を二量化することが可能であることを確認した。

実施例25

ゲスト分子の光二量化反応を用いた光記録媒体(3)

ホスト分子として No.53のジアセチレンジオール、ゲスト分子としてケイ皮酸を用いて、実施例1と同様の操作により単分子膜及び、これを3，5，9，15，19層に累積した。単分子層累積膜を記録層とする光記録媒体を製造した。次に高圧水銀灯を用いて、これらの膜を全面露光して、ゲスト分子を二量化（式Ⅵ）、ホスト分子を重合（式Ⅴ）させた後、パターンに従って、波長270 nmの紫外光を照射して、ゲスト分子を解重合させて情報を記録した。分子オーダーの記録が可能であった。



（Ⅵ）

記録の再生は、二量化したゲスト分子の解重合に伴う波長380 ～420 nm付近の吸収変化を読み取る事により行った。

更に再び高圧水銀灯を用いて上記記録媒体を全面露光することにより記録を消去することが可能であることを確認した。なお一度高圧水銀灯で全面露光した本記録媒体を、アルコール中に約30秒間浸漬した後、上記方法により情報の記録／再生を行ったが、特に問題点はなかった。即ち、ホスト分子を重合させる事により該記録媒体の化学的強度が大となることが確認された。

実施例26，27

ホスト分子として No.53のジアセチレンジオール、ゲスト分子としてアントラアルデヒドをモル比1：2の割合でクロロホルムに溶かし、実施例1と同様に操作により単分子膜及びこれを5，9，15，31，60，80層に累積した単分子層累積膜を記録層とする光記録媒体を製造した。

作成した光記録媒体にパターンに従ってX線照射を行ない、式（Ⅳ）に示すゲスト分子の二量化反応を行ない情報を記録した。分子オーダーの記録が可能であった。記録の再生はゲスト分子の二量化に伴う波長370 ～ 390nm付近の吸収変化を読み取る事により行った。次いで、波長 313nmの紫外光を1時間照射したところ解重合が起こり、記録の消去が可能であることを、確かめた。

No.41のアントラセン誘導体を用いた場合にも同様の結果を得た。（実施例27）

実施例28

ゲスト分子の昇華を利用した記録媒体(1)

ホスト分子として、No.54のアセチレンジオールをクロロホルムに溶かした後、pH6.5，塩化カドミウム濃度 4×10^{-4} Mの水相上に展開させた。溶媒のクロロホルムを蒸発除去させた後、系の気相側をアセトンで飽和させた。このアセトン雰囲気下、表面圧を35dynes/cmにまで高めて包接錯体を膜状に析出させた後、気相側のアセトンを空気若しくは窒素で置換した。次いで、表面圧を一定に保ちながら、表面が十分に清浄なガラス基板を上下速度2cm/min で水面を横切る方向に静かに上下させ、単分子膜を基板上に移しとり、単分子膜及び3，5，9，15，19，40，60，80，80 層に累積した単分子層累積膜を記録層とする記録媒体を製造した。この累積行程に於いて、基板を水相から引き上げる際度に30分間以上放置して基板に付着している水分を蒸発除去した。成膜装置としては、英国 Joyce 社製の Langmuir-Trough 4 を使用した。

炭酸ガスレーザ又は赤外線レーザーを用いて作成した記録媒体にパターンに従ってレーザ光を照射したところ、照射部位だけゲスト分子、即ちアセトン分子が、気化除去され、その部分の吸収スペクトル強度（入max=280nm）が減少し、情報の記録が成された。分子オーダーの記録が可能であっ

た。又、ゲスト分子の与奪をシュリーレン法を用いて読みとることによる記録再生方法も可能であった。この記録媒体をアセトン気流中に1時間放置したところ、アセトンの除去された部位に再びアセトンが包接され、記録が消去されると共に、再記録が可能であった。この記録消去－再記録のプロセスは少なくとも数十回の使用に耐え、反復使用が可能であることを確認した。

実施例29～32

実施例28のホスト分子 No.54の代わりに No.49～ No.52を用いた場合にも実施例27と同様の結果が得られた。

実施例33～38

ゲスト分子の昇華を利用した記録媒体(2)

ホスト分子として No.49～ No.52を用い、クロロホルムに溶かした後、pH6.5、塩化カドミウム濃度 4×10^{-4} Mの水相上に展開させた。この際、系の気相側をクロロホルムでほぼ飽和させた。溶媒（疎側）のクロロホルムがほぼ気化するのを待って（約5分）、表面圧を35dynes/cmにまで高めて包接錯体を固体状に析出させた後、気相側のクロロホルムを空気、若しくは窒素で置換した。次いで、表面圧を一定に保ちながら表面が十分に清浄なガラス基板を上下速度、2cm/minにて水面を横切る方向に静かに上下させ、単錯体分子膜を基板上に移しとり、単錯体分子膜及び3、5、9、15、19層に累積した単錯体分子層累積膜を記録層とする記録媒体を製造した。

炭酸ガスレーザ又は赤外線レーザーを用いて作成した記録媒体にパターンに従ってレーザ光を照射したところ、照射部位だけ、ゲスト分子、即ちクロロホルムが、気化除去され記録が成された。分子オーダーの記録が可能であった。このゲスト分子の部分的除去に伴う膜の形状変化をシュリーレン法を用いて読みとることにより情報の再生が可能であった。該記録媒体をクロロホルム気流中に1時間放置したところ、クロロホルム分子が再包接され、記録が消去されると同時に再記録が可能であった。この記録消去－再記録のプロセスは、少なくとも数十回の使用に耐え、反復使用が可能であることを確認した。

なおゲスト分子及び展開溶媒として、ベンゼン(No.45、実施例37)、ジクロルメタン(No.46、実施例38)を用いた場合にも同様の結果を得た。

実施例39～44

ゲスト分子の昇華を利用した記録媒体(3)

ホスト分子として No.49～ No.52、ゲスト分子として1,2-エポキシプロパン(NO.43)を用いて実施例26と同様にして単錯体分子膜乃至、単錯体分子層累積膜を記録層とする記録媒体を製造した（実施例39～42）。この際、予め水相側に1,2-エポキシプロパン(No.43)を 1～10M程度溶解させて、気相側のゲスト分子が、水中に拡散するのを防止した。情報の記録、再生、及び消去の方法並びに結果は実施例28と同様であった。

なお、ゲスト分子としてアセトン、エチレンイミン(No.44)を用いた場合も同様の結果を得た。（実施例43～44）。

実施例45～48

ゲスト分子の昇華を利用した記録媒体(4)

ホスト分子として No.49～ No.52、ゲスト分子として臭化メチル No.48を用いて実施例26と同様にして単錯体分子膜乃至単錯体分子層累積膜を記録層とする記録媒体を製造した。情報の記録、再生及び消去の方法並びに結果は実施例28と同様であった。

実施例49～55

ゲスト分子の昇華を利用した記録媒体(5)

ホスト分子として No.53を用い、ゲスト分子に No.42～ No.48を用いて単錯体分子膜乃至3、5、9層に累積した単錯体分子層累積膜を作成した。この作成方法はゲスト分子の種類によって、若干異なり、実施例26～44に記した方法により作成した。かかる単錯体分子膜乃至単錯体分子層累積膜を高圧水銀灯を用いて全面露光してホスト分子を重合させて記録媒体を製造した。

情報の記録、再生、及び消去の方法並びに結果は、実施例26或いは実施例28と同様であった。本方法によればホスト分子の基板付着力が、実施例26～44に比べて、増大する。従って記録媒体の化

不飽和度が相対的に大となり、反復使用回数をなくとも100回まで増大できることがわかった。

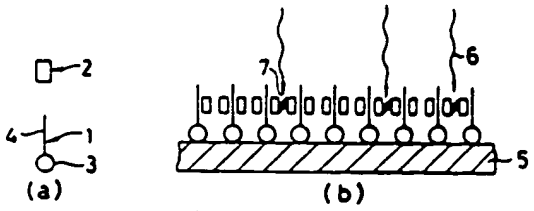
第1表

	基本骨格	
No.49	No.10	m = 9 , n = 2
No.50	No.2.	Z=COOH, n = 2
No.51	No.15	m = 9 , n = 2
No.52	No.30	Z=COOH, n = 4
No.53	No.7	m = 8 , n = 8
No.54	No.4	m = 9 , n = 2

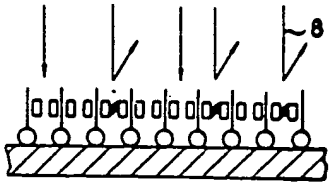
4.図面の簡単な説明

第1図～第3図は、本発明に係る重合成膜体の実施例を説明する概略断面図であり、各々、第1図は記録過程、第2図は再生過程、第3図は消去過程を示しており、第4図～第5図は本発明に係る包接錯体の水相上における状態を説明する説明図である。

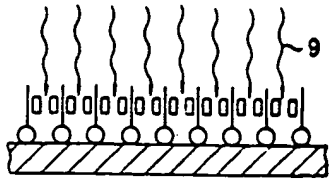
1 --- ホスト分子　　2 --- ゲスト分子
3 --- 親水性部位
4 --- 長鎖アルキル部位
5 --- 基板
6 --- X線
7 --- 二量化部位　　8 --- 可視光
9 --- 紫外線
10, 11--- 包接部位
12, 13--- 被包接部位
14--- 長鎖脂肪酸部位
15--- 親水性部位
16--- 水相



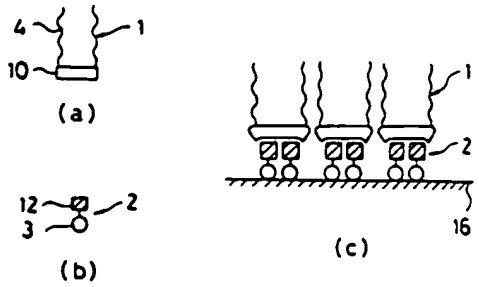
第 1 図



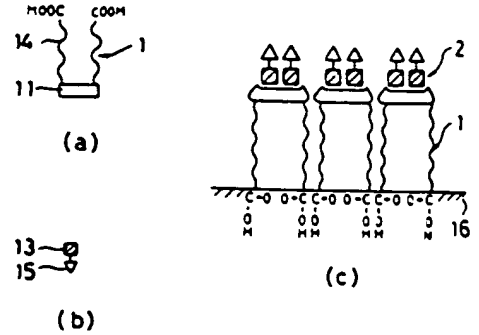
第 2 図



第 3 図



第 4 図



第 5 図